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THE ELECTROCHEMISTRY OF LIGHT. IV

BY WILDER D. BANCROFT

The Problem of Solarization. Part I

The literature on the subject of solarization or the reversal of the photographic image is so scattered and to a certain extent so contradictory that it has seemed wise to give a pretty thorough idea of the problem in two papers and to postpone till a later paper the application of the theory of Grotthuss to this problem.

There is an excellent presentation of certain portions of the subject to be found in a lecture by Major-General Waterhouse,[1] which was delivered on April 14, 1901, and from which I quote extensively.

"The observation of the reversal or apparent destruction of the impressed photographic image was a very early one in the history of photography. Early in 1801, Ritter showed that silver chloride, which had already been darkened in the violet rays of the spectrum, became lighter again when exposed to the yellow, red, and especially the infrared rays, and he attributed this to an oxidizing action of the less refrangible rays counteracting the deoxidizing action of the more refrangible rays.[2] Wollaston,[3] on the other hand, shortly afterwards, in 1804, stated that about the same time as Ritter, he had found that while gum guaiacum became green by oxidation when exposed to the violet rays, it was deoxidized and brought back to its original yellow color by the red and orange rays. The same decolorizing effect could, however, also be produced by heat. Much later, in 1840, Sir John Herschel[4] described a similar experiment in which, again, paper coated with the alcoholic tinc-

[1] Jour. Camera Club, **15**, 63 (1901).
[2] Phys. Chem. Abhandlungen, **2**, 90.
[3] Nicholson's Journal, **8**, 293 (1804).
[4] Phil. Trans., **130**, 35 (1840).

ture of guaiacum was first exposed to light, and then exposed in the spectrum, the result being that the part acted on by the more refrangible rays became of a darker blue than the original ground, while about the orange rays the original pale yellow color of the paper was restored.

"In 1842, J. W. Draper, by allowing daylight to fall along with the spectrum upon a Daguerreotype plate, found that the daylight and sunlight antagonized each other, and thus he succeeded in obtaining the first photograph of the red end of the spectrum showing the α, β and γ lines below A, these lines appearing positive.

"This bleaching action of the red and orange rays upon sensitive surfaces already darkened or affected by exposure is very remarkable when taken in connection with the opposite effect which can be produced on under-exposed Daguerreotype or paper prints prepared with haloid salts of silver containing an excess of nitrate, by continuing the exposure under a yellow or red glass. This continuing action of the less refrangible rays was discovered in 1840 by Edmond Becquerel, and led him to call the more refrangible rays *rayons excitateurs*, and the less refrangible *rayons continuateurs*. It can be shown quite well with P.O.P.,[1] or an iodized silver plate.

"It is noteworthy that Ritter, in discussing the nature of the difference between the action of the two ends of the spectrum, says that water is the chemical agent in all processes of oxidation in the wet way, and that it is decomposed in all processes of oxidation or deoxidation. In the first case, the oxygen combines with the oxidizable body, and the hydrogen is set free or combines with more oxygen to form water anew. In the second case, the hydrogen of the water combines with the oxygen of the body to form water, while the oxygen formerly combined with the hydrogen goes to the oxidizable body present, the deoxidation of which it usually only indirectly brings about. In some later

[1] [Printing out paper.]

researches he showed that perfectly dry silver chloride is not acted on by white light, or the violet rays.

"Some years, however, before Ritter announced this theory in connection with photographic action, our own countrywoman, "the ingenious and lively" Mrs. Fulhame, as Count Rumford calls her, had discovered, and published[1] in 1794, that the presence of water is essential to the reduction of metals (more especially the salts of gold and silver) by light, an observation which has been confirmed so far as most of our ordinary photographic processes are concerned. She held that when light reduces the metals, it attracts the oxygen of the water, while the hydrogen of the latter unites in its nascent state to the oxygen of the metal and reduces it, forming, at the same time, a quantity of water equal to that decomposed. Further, she says, water is decomposed in every instance of oxygenation.

"Ritter[2] wrote an analysis of Mrs. Fulhame's book and thus was well acquainted with her theories, some of which he seems to have adopted. He himself made a good many observations on the action of light, and intended to have devoted himself to the study of it, but was led to give most of his energies to the development of galvanism. This study led him to remark in one of his numerous papers that the result of a thorough practical investigation would be that the polarity of chemistry, electricity, magnetism, heat, etc., was due to a single principle common to all. He was also one of the first to recognize the electrical nature of sunlight. Eder says, however, that his hasty and unverified electrical hypotheses led him astray.

"Experiments made long after Ritter's, by Robert Hunt, also showed that the accelerating power of moisture in promoting the reduction of silver salt was due to the decomposition of the water and the formation of nascent hydrogen. Schönbein has also shown that, in all cases of oxidation, in presence of water, hydrogen peroxide is formed. It is well

[1] Essay on combustion.

[2] Phys. Chem. Abhandlungen, 1, 91.

known that this substance is capable of acting both as an oxidizer and a reducer, and as Sonstadt has found traces of it when silver chloride is exposed to light in water, it is probable that it has to be reckoned with in most cases of photographic action.

"I have dwelt on these early researches of Mrs. Fulhame and Ritter, because the principles they enounced as to the action of moisture in the reduction of silver and gold from their salts by the action of light seems to be closely connected with the phenomena of photographic reversals, which it is generally agreed are due to oxidation, though they do not fully represent the complex actions that take place in our ordinary photographic processes.

"The lightening action of the less refrangible rays of the spectrum upon darkened silver chloride was confirmed in 1810 by Seebeck, who also recorded some interesting observations on the differences of tint taken by silver chloride exposed under colored glasses, corresponding with the color of the transparent medium under which it was exposed. With this aspect of the question we have, however, nothing to do.

"The next process of reversal to be noticed is one that appears to have been first published by Dr. Fyfe,[1] in April, 1839, though several similar processes for obtaining positive pictures direct in the camera were brought out all about the same time, in 1839 and 1840, by Bayard and Lassaigne in France, and by Herschel, Hunt and Talbot in England.

"In Fyfe's process, paper prepared with silver phosphate (in most of the other processes silver chloride was used) was first darkened by the action of light, then immersed in a solution of potassium iodide, and while still moist, exposed to light in contact with the object to be reproduced, and left until the whole of the paper exposed became yellow. It thus showed a positive image of the subject, dark upon a light ground. The prints were fixed by simple washing in water

[1] Phil. Mag. [3], 14, 463 (1839).

to remove the soluble iodide. He also stated that darkened silver chloride could be used, but with a weaker solution of iodide.

"Robert Hunt, in his *Popular Treatise on the Art of Photography*, published in 1841, has given a full account of this method, and has discussed the principles on which the action is based. He says, "If a dark paper is washed with an hydriodate (iodide in solution), and exposed to sunshine, it is first bleached, becoming yellow, then to light again darkens it. If, when quite dry, it is carefully kept from the light, it will be found in a few days to be again restored to its original yellow color, which may be again darkened by exposure, and the yellow color be again restored in the dark. The sensitiveness to the influence of light diminishes after each exposure, but I have not been able to arrive at the point at which this entirely ceases. If a dark paper, bleached by an hydriodate (iodide) and light, be again darkened, and then placed in a bottle of water, the yellow is much more quickly restored, and bubbles of gas will escape freely, which will be found to be oxygen. By enclosing pieces of hydriodated (iodized) paper in a tube to darken, we discover, as might have been expected, some hydrogen is set free. If the paper is then well dried, and shut up in a warm dry tube, it remains dark; moisten the tube or the paper, and the yellowness is especially restored.

"Take a photograph thus formed and place it in a vessel of water, in a few days it will fade out, and bubbles of oxygen will gather around the sides. If the water is examined, there will be found no trace of either silver or iodide; thus it is evident that the action has been confined to the paper.

"We see that the iodide of silver has the power of separating hydrogen from its combinations. In the process of darkening, the liberation of hydrogen is certain, but I have not in any instance been able to detect free iodine; of course it must exist, either in the darkened surface or in combination with the unaffected under layer; possibly this may be

the iodide of silver with iodine in simple mixture, which, when light acts no longer on the preparation, is liberated, combines with the hydrogen of that portion of moisture which the hygrometric nature of the paper is sure to furnish, and as an hydriodate again attacks the darkened surface restoring thus the iodide of silver. This is strikingly illustrative of the fading of the photograph.

"The picture is formed of iodide of silver in its light parts, and of oxide of silver in its shadows. As the yellow salt darkens under the influence of light, it parts with its iodine, which immediately attacks the dark oxide, and gradually converts it into an iodide. The *modus operandi* of the restoration which takes place in the dark is not quite so apparent. It is possible that the active agent *light* being quiescent, the play of affinities comes undisturbed into operation —that the dark parts of the picture absorb oxygen from the atmosphere, and restore to the lighter portions the iodine it has before robbed them of." Hunt then describes a series of experiments on silver iodide which more strikingly exhibit this remarkable peculiarity.

"He repeats the above in his later work published in 1859, and I have quoted it at length because it seems to give a very probable exposition of the reactions which take place in some reversals and carries on the theory enunciated by Mrs. Fulhame and Ritter of photographic action being to some extent dependent on the decomposition of water present either in the atmosphere or in the sensitive surface.

"On the same principle, Poitevin proposed in 1859 a method of obtaining reversed positives in the camera which seems to have been successful in his hands for making stereoscopic transparencies.

"A sensitive plate was prepared by the wet collodion process, with a collodion containing less iodide than usual for negatives. It was then exposed for a few seconds to direct light, the appearance of the plate being unchanged. After washing to remove the excess of silver nitrate, it was treated with a 4 percent solution of pure potassium iodide

free from iodine, all these operations being performed in the dark room. The plate was then exposed in the camera about three times longer than the ordinary exposure for negatives. It was next washed to remove the iodide solution, and having been treated with a weak bath of silver nitrate at 2.5 percent, was developed with pyrogallic acid, acidified with lactic acid. It was then blackened only in the parts acted on by light, and after the development had been carried to the usual extent, the image was fixed with a weak solution of hyposulphite or cyanide, or a mixture of the two. The image obtained in this manner was a positive by transparence.

"Poitevin[1] gives a list of substances which he found might replace the potassium iodide in bringing about this reversing action—among them those most active were: cyanide of potassium, also when saturated with silver iodide; solution of bichromate of potash acidified with sulphuric acid; dilute hydrochloric acid.

"Sir William Abney has given the rationale of this process in his *Treatise on Photography*, p. 305, and has shown that potassium or other simple bromide can be substituted for the iodide.

"He also shows that if a plate prepared with silver iodide have a preliminary exposure given to it, and then be given a prolonged exposure in the camera, reversal of the image will take place. If, however, such a plate, after washing, be treated with a solution of a deoxidizing agent, such as pyrogallic acid or potassium nitrate, the reversal will not take place, nor will it if the plate be exposed in a cell containing a hydrocarbon such as benzene, or in dry hydrogen. Consequently, the presence of oxygen in some form is necessary to obtain reversal, and it is not easily obtained if a substance readily taking up oxygen is in contact with the silver salt.

"In 1862, Dr. Sabatier[2] gave a description of a method

[1] Traité de l'impression photographique sans sels d'argent, p. 117ff.

[2] Phot. News, 6, 366 (1862).

of obtaining direct positives in the camera. A glass plate was coated with a bromoiodized collodion, sensitized in a neutral silver bath, and given a normal exposure in the camera. The plate was developed with weak pyrogallic acid solution, acidified with glacial acetic acid. As soon as the details were out, the developer was poured off, and the plate washed. It was then treated with a 4 percent solution of silver nitrate, which was again poured off after a sufficient interval, and then the plate was redeveloped with the pyrogallic acid solution, the development of the positive image taking place quickly if the treatment with the silver solution had been prolonged—more slowly with a shorter treatment or a weaker silver solution. The plates were fixed in hypo or cyanide, and could be toned if desired.

"The most interesting feature of this process is Dr. Sabatier's theory of the reversal of electrical action by the second silver bath. He says: "When no more pyrogallic acid remains on the plate, the formation of the negative must necessarily be interrupted, and to form a color different from the first with the exposed iodide not yet employed, it suffices to substitute for the electrical current which prevailed at the first combination, an electric current of the opposite nature.

"Many substances poured in solution upon a negative, the formation of which has been interrupted, possess the power of inverting the electrical current previously developed, and causing the positive combination to succeed the negative. Such are most of the alkalis, limewater, solution of ammonia, and especially nitrate of silver." "The presence of strong acids in the bath or developing solutions was prejudicial, and, therefore, preference was given to pyrogallic acid with acetic acid which does not interfere with the transformation.

"The difficulty, of course, is in knowing when to stop the first development, but Dr. Sabatier says that, with the method he described, successful results were obtained. At any rate, the theory of the reversal of current working the

transformation from negative to positive is of interest, though rather vague. It was founded on some observations of the Abbé Despratz, which are given in the same volume. Another method of Sabatier's was by admitting light after the development was started; the light acting on the developed parts caused them to blacken at the expense of the already partially developed parts. Many similar methods with wet collodion will be found in the journals, and are referred to by Eder, in his *Ausführliches Handbuch.*[1]

"Returning to the earlier periods, we note that shortly after the introduction of the Daguerreotype process it was found that if the exposure of the plates in the camera was unduly prolonged, the mercury was deposited irregularly over the plate, giving a pale blue image, with a partial or total reversal. Dr. J. W. Draper was, I think, the first to study this phenomenon, and he attributed it to an action of the rays of light analogous to those of heat acting on a mass of ice, the temperature rising gradually to 32° F, where it stops till the molecular change of liquefaction is accomplished, when it goes on rising again. In the same way, when the rays of light begin to act on a Daguerreotype plate, the silver iodide commences changing, and is capable of being whitened by mercury. This process goes on gradually with increased whiteness on the more exposed parts until a certain point is gained, when the iodide apparently undergoes no further visible change, but another point being gained, it begins to assume, when mercurialized, a pale-blue tint, becoming deeper and deeper, until at last it assumes the

[1] I find that in 1888 a series of experiments was made in the Photographic Office, S.I.D., Calcutta, with Poitevin's, Sabatier's, and other processes of making reversed positives with wet collodion, with the result that the only one likely to be of practical use was that described by Capt. Biny, in the *Bull. Soc. Franç. de Photographie*, 27, 130. With gelatine dry plates, it was found hyposulphite of soda in the developer, or preliminary treatment of the plates with bichromate of potash seemed to have little influence in causing reversal. The best reversals were obtained by a simple over-exposure of about 1,800 times normal, or 30 minutes for an "ordinary" plate. This agrees with results lately obtained by Dr. R. Englisch.

brilliant blue of a watch-spring, thus producing the effect called solarization.

"He gave no further elucidation on physical or chemical grounds at the time, but in a later paper[1] he maintained that the plate was polarized to light. He says, 'We know that iodine is not thrown off during exposure, but is absorbed by the underlying silver, while silver is liberated on the anterior surface of the plate. From the circumstance that iodine is evolved at the back of the film and silver at its front, the film itself remaining of the same thickness throughout, it is obvious that there is a strong resemblance between this phenomenon and that of the polar decomposition of water. The electro-positive and electro-negative elements are yielded up on opposite faces of the film, and its interior undergoes incessant polar changes, the opposite electrical particles sliding, as it were, on one another.'

"There is, I think, little doubt that some such action does take place; during the exposure there is a constant transference of atoms, till after a certain stage there is an excess of silver in the most exposed parts, and the mercury is deposited more readily upon the less exposed parts, or more or less equally all over the plate.

"Draper also found the Daguerreotype plates were acted on by the red and blue rays of the spectrum, in opposite ways, similarly to the action noticed by Ritter with silver chloride.

"Moser also examined the phenomenon of the solarization of Daguerreotype plates, and attributed the gradual change in the developable condition of the iodized silver surface to the action of atmospheric oxygen, which is ever present and cannot be gotten rid of. This agrees with Scholl's theory, referred to in my lecture on the *Teachings of Daguerreotype*, that there is a constant transference of atoms by the continual formation of silver oxide and silver iodide, their alternate decomposition and re-formation. The same prin-

[1] Phil. Mag. [3], **22**, 367 (1843).

ciple probably applies to gelatine dry plates, in which, however, moisture diffusing through the colloid material, no doubt plays a very active part.

"During the course of recent work on Daguerreotype, I found that plain metallic silver exposed to light showed this reversed action by long exposure very distinctly when developed with mercurial vapor, and I had several instances of it, some of which I can show you. In this case, of course, there is no halogen or electro-negative element present except the atmospheric oxygen, together with the moisture of the air. How far the change in the molecular structure of the film may be due to their action I am not prepared to say, but, as far as I have been able to ascertain, metallic silver is not oxidized by exposure to light, and any action would more probably be catalytic, as in the case of the iodide, according to Scholl's theory.[1]

"In 1875, during the course of some experiments in photographing the solar spectrum on dyed collodio-bromide dry plates, I constantly met with reversals in the red or blue end of the spectrum, often both simultaneously. Noticing that when the plates were quite clear of fog the reversal at the red end did not take place, while the direct action only extended as far as C, and recollecting Draper's principle of previous exposure of the plate, I was able to obtain a reversed negative picture of the whole of the red spectrum up to and some little distance beyond A. In this case the lines appeared black on a clear ground, and the plates were stained blue with a mixture of malachite green and methyl violet, known as "marine blue," but similar results were also obtained with plates stained with annatto, as well as with other coloring matters and aniline dyes.

"By another application of the same principle I found that very complete reversed negatives could be obtained by first exposing one of these stained dry plates for a short time to light, and then placing it in a printing frame under

[1] Wied. Ann., 68, 149 (1899).

a negative, over the face of which a red glass was placed. After an exposure in the sun for about twenty minutes and developing with alkaline pyro a very fair negative was produced.

"When exposed under blue glass, however, these plates gave quite a mixed result, half positive and half negative. It is not impossible that suitable gelatine dry plates treated in the same way would produce similar results, and such a method would have many practical uses. I am sorry I have no specimens of the method to show you, but I have brought with me two of the collodio-bromide plates of the spectrum, one stained with a blue dye and the other with naphthalene red.

"In April, 1876, when photographing the sun on similar blue-stained collodio-bromide plates, I had a case of recurrent reversal, but not to its full extent, of which an account is given in the *Phot. Journ.*, May, 1898. One of these plates showed, with an almost instantaneous exposure, an unreversed image; exposures of 5 to 10 seconds were fully reversed, and then as the exposures increased from 60 to 80 up to 200 seconds, the reversal was not observed except just round the limb. The reversed images were all quite clear and sharp. With an unstained plate, the reversed images were those exposed for the shortest time, and then they gained strength according to the length of exposure. With similar plates prepared with collodion containing annatto, the shorter exposures were well reversed, then, as the exposure increased, the images of the sun were not so clear, but cleared again as longer exposures from 100 to 200 seconds were given.

"In 1879, Bennett[1] stated that gelatine dry plates were very readily reversed by over-exposure, and showed this phenomenon of recurrent reversal very clearly, the image first gaining intensity up to a certain point, then losing it by over-exposure, to a point when the most exposed parts are perfectly clear on development, then increasing in den-

[1] Phot. News, 23, 139 (1879).

sity again, and then again losing it. Sir William Abney has shown that in this case, also, the tendency to reversal is destroyed by exposing the plate bathed with a solution of potassium nitrite, while a solution of potassium bichromate will favor it.

"In 1880, M. Janssen carried the observation of these recurrent reversals much further, and, by prolonged exposure, obtained six distinct stages.

1. The ordinary negative image.
2. The first neutral state, dark ground.
3. The positive image.
4. The second neutral state, clear ground.
5. The second negative.
6. The third neutral state, dark ground.

The second negative was calculated to require 100,000 times normal exposure."

From a paper by Draper[1] I quote the following paragraphs:

"The accompanying photographic impression of the solar spectrum, which I will thank you to give to Sir John Herschel, was obtained in the south of Virginia—probably you can make nothing like it in England, the sunlight here in New York wholly fails to give any such result. It proves, that under a brilliant sun, there is a class of rays commencing precisely at the termination of the blue, and extending beyond the extreme red, which totally and perfectly arrest the action of the light of the sky. This impression was obtained when the thermometer was 96° Fahr. in the shade, and the negative rays seem almost as effective in protecting, as the blue rays are in decomposing iodide of silver.

"The most remarkable part of the phenomenon is that the same class of rays makes its appearance again beyond the extreme lavender ray. Sir J. Herschel has already stated, in the case of bromide of silver, that these negative rays exist low down in the spectrum. This spectrum, how-

[1] Phil. Mag. [3], 21, 349 (1842).

ever, proves that they exist at both ends, and do not at all depend on the refrangibility. It was obtained with yellow iodide of silver, Daguerre's preparation, the time of exposure to the sun fifteen minutes.

"In this impression, six different kinds of action may be distinctly traced by the different effects produced on the mercurial amalgam. These, commencing with the most refrangible rays, may be enumerated as follows:—1st, protecting rays; 2nd, rays that whiten; 3rd, rays that blacken; 4th, rays that whiten intensely; 5th, rays that whiten very feebly; 6th, protecting rays.

"It is obvious we could obtain negative photographs by the Daguerreotype process by absorbing all the rays coming from natural objects, except the red, orange, yellow, and green, allowing at the same time diffused daylight to act on the plate.

"This constitutes a great improvement in the art of photography, because it permits its application in a negative way to landscapes. In the original French plan the most luminous rays are those that have least effect, while the sombre blue and violet rays produce all the action. Pictures, produced in this way, never can imitate the order of light and shadow in a colored landscape.

"If it should prove that the sunlight in tropical regions differs intrinsically from ours, it would be a very interesting physical fact. There are strong reasons to believe it is so. The Chevalier Fredrichstal, who traveled in Central America for the Prussian government, found very long exposures in the camera needful to procure impressions of the ruined monuments of the deserted cities existing there. This was not due to any defect in his lens; it was a French achromatic, and I tried it in this city with him before his departure. The proofs which he obtained, and which he did me the favor to show me on his return, had a very remarkable aspect. More recently, in the same country, other competent travelers have experienced like difficulties, and as I am informed failed to get any impressions whatever. Are

these difficulties due to the antagonizing action of the negative rays upon the positive?"

This paper of Draper's brings up two points, the reversing action of certain rays and the apparent necessity for long exposures in tropical countries. The second part was answered by Beck[1] in 1904, though no reference was made in the latter's paper to the question asked by Draper. Beck's observations are so interesting that I take the liberty of quoting them even though they have no direct connection with the problem of solarization.

"The first time I set up my camera in Egypt I was startled at the way in which the picture looked on the focusing screen. Instead of a beautiful harmonious image it looked like a harsh photograph. There were crude, bright lights and immediately adjoining them, almost without intermediate steps, were deep, black shadows showing almost no details. It was clear to me at once that, in spite of all theory, a short exposure was out of the question. In fact, on account of the deep shadows, it would be necessary to give a longer exposure than would be customary under the same conditions at home (Vienna).

"After thinking the matter over for a while I saw clearly what was the cause of the great contrasts and especially of the heavy dark shadows. I perceived that the purer air of the South—just because of its clearness and permeability to light—did not scatter the sun's rays so much as our own air does. Since the shadows were lighted so little by diffracted light, they were necessarily heavier and darker than they would have been in our latitudes.

"The phenomenon of the dark black shadows appeared in the most surprising way in the dry, crystal-clear, desert air of Upper Egypt.

"For three weeks, while I was partly on the Nile and partly in the desert, I had absolutely no chance to develop any plates, but I was nevertheless so convinced of the ac-

[1] Eder's Jahrbuch der Photographie, **18**, 159 (1904).

curacy of my observations that in practically every case I made longer exposures than were permissible theoretically. The results were an eminently satisfactory confirmation of my views. In view of all this[1] and as a consequence of similar experiences in Africa, Spain, Greece and elsewhere, I should sum up my experiences in regard to length of exposure in southern countries as follows:

"In southern countries a relatively brief exposure is permissible only when practically all parts of the subject to be photographed are well lighted. If large or important portions are in shadow, a shorter exposure will not do and one must expose at least as long as, and in very clear, dry air up to twice as long as, one would do at home under equally favorable conditions of light. Of course, this is after taking into account variations due to the differences in the season, length of day, and height of sun, resulting from the difference between our latitude and that of the southern country."

Waterhouse referred to Abney's work on reversals, but Abney's paper[2] is of such fundamental importance that I quote it practically in full.

"It is well known, if a plate be prepared with silver iodide by the ordinary wet process, be briefly exposed to light, and after washing be treated with a solution of potassium iodide and then be exposed to an image in the camera, that, after dipping in the silver-bath and developing, a positive image is obtained. It matters not whether the potassium iodide be alkaline, neutral, or acid, the same effect will be noted; also that there is no difference if, after treatment with the potassium iodide, the plate be washed or not, the reversal of the image will still be shown. In this case the iodine is liberated as before, but the action is increased by the access of oxygen from the air; in fact it is a mixture of effects.

"If potassium bromide or any simple bromide be substi-

[1] Cf. Wiener Phot. Blätter, 1898, 267; Phot. Correspondenz, 1899, 45.
[2] Phil. Mag. [5], 10, 201 (1880).

tuted for the iodide, the same result obtains. Silver iodide, if prepared with an excess of soluble iodide, or if, after preparation with excess of silver, it be treated with a soluble bromide, is insensitive to light, and the explanation of this perhaps may be found in the fact already stated.

"It has been usually held that a soluble iodide, such as potassium, can destroy an invisible impression made by radiation, but this is not the case if it be treated with the iodide in the dark. If, however, any iodide, such as cupric or ferric, be employed, which readily liberates an equivalent of iodine, the destruction is accomplished in the dark. The least favorable iodides for such destruction, as I have already shown,[1] are the monads.

"If a plate prepared with silver iodide have a preliminary exposure given it, and then be exposed *for a considerable time* to the image formed in the camera, a reversal of the image will take place as before. If, however, such a plate, after washing, be treated with an aqueous solution of pyrogallic acid, potassium nitrite, or any other oxidizing agent, such reversal of the image will not be obtained; nor will it if it be exposed in a cell containing such a substance as benzene, or if exposed in dry hydrogen. From this we learn that, to obtain reversal, oxygen must be present in some form or other, and that if a substance readily taking up oxygen be in contact with the silver salt, a reversal cannot be readily obtained.

"An interesting corroboration of the above statement is to be found in the treatment of an exposed plate in a cell containing a dilute solution of permanganate of potash, bichromate of potash, or hydroxyl, when it will be found that the reversal takes place with the greatest facility. The same reversals may also be obtained by using any of the mineral acids in a diluted form.[2]

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[1] Photographic Journal, 1878.

[2] It must, however, be remembered that the solutions must be very dilute, or the whole effect of the preliminary exposure will be destroyed, since these oxidizing agents are active in the dark, but act more readily in the light.

"The above experiments show, then, that a reversal may be obtained by the presence of the iodides or bromides (and in a more feeble manner I have also found, by that of the chlorides), and also by oxidizing agents and mineral acids, while the presence of a deoxidizing agent, or the exposure of the plate in a medium free from oxygen, prevents the occurrence of the phenomenon.

"We shall consider shortly as to whether the reversing action depends upon the sensitiveness of the salt of silver obtained by the preliminary exposure, or upon that of the agents employed in effecting such reversal.

"With the bromide of silver we have rather different phases of the phenomenon to consider. The development can be carried out with the alkaline or the ferrous oxalate developer, a mode which is more easy to carry out than the development by precipitation of metallic silver from an aqueous solution of silver nitrate. For experimental purposes, films containing silver bromide may be formed of collodion or of gelatine, and the behavior of the silver salt in the two vehicles is somewhat different, and has to be considered separately. Collodion is, or should be, a strictly neutral substance; that is, it is merely a medium in the pores of which the silver salt is entangled and kept in position, and has no effect on the progress of development or on the action of light, beyond that which may be due to its physical qualities, its chemical constitution remaining unchanged.

"A collodion film is essentially porous and not continuous, as may be seen by a microscopic examination, and free access of the atmosphere to the silver is thus obtained. Gelatine, on the other hand, is a substance readily acted upon by oxidizing agents and by the halogens; and consequently it may have an effect on the progress of development and on the action of light, its chemical constitution becoming altered. It is a homogeneous film, and not porous in the ordinary sense of the word, and is a protective agency against the atmosphere to those silver salts which may be embedded in it.

"The most convenient method of experimenting with silver bromide is in the form of emulsion, made either with collodion or with gelatine, but it is not to the purpose of the present paper to refer to the mode of preparation beyond stating that in the former case the emulsion is usually prepared with an excess of silver nitrate, and the latter with an excess of soluble bromide, both of which are eliminated as far as possible by washing.

"If a film containing silver bromide, whether in gelatine or collodion, have a preliminary exposure given to it, and then be treated with a soluble bromide of an alkali, such as of potassium, and be again exposed to light in the camera, it will be found that there is not such a rapid reversal of the image as with the iodide, but that longer exposure is required to effect it, the reason being that bromide of silver prepared with a large excess of soluble bromide is still sensitive to light. If, therefore, the light decomposes the soluble bromide on the plate, liberating enough bromine to form fresh bromide of silver with the subbromide formed by the preliminary exposure, that freshly formed bromide, being sensitive to light, is again reduced to the subbromide state by the same rays which formed it. It will be evident, however, that reversal should take place more rapidly with the soluble bromide present than without it, and such is the case.

"It is useless to treat a silver bromide film with a soluble iodide, since silver iodide is immediately formed, and the reactions that take place are similar to those already described.

"If bromide of silver in collodion be exposed to the image in the camera without the presence of any other substance, a reversal takes place. Roughly speaking, the reversal takes some sixty times more exposure to the light than is requisite to produce the maximum ordinary effect. To trace the cause of this reversal it is only necessary to treat the film with a 5 percent solution of potassium nitrate, when it will be found that the reversal does not take place. The

same holds true when the film is treated with any deoxidizing solution, or if the plate be immersed in benzene or hydrogen. The cause, then, of the reversal in this case is evidently an oxidation, and this may be further verified by treating the film, after a preliminary exposure, with bichromate of potash, hydroxyl,[1] etc.; it will then be found that the reversal takes place much more rapidly than when those oxidizing agents were absent. The same may be said of the mineral acids.

"If silver bromide be held in a gelatine film, the action of light is somewhat different. If the plate be exposed in the camera for a short time, say a few seconds, the image develops in the usual manner and we have a negative image; if it be prolonged to, say, a minute, the image is reversed on development; a further exposure causes a negative image to be produced, while one much more prolonged causes a positive image again to be formed on development. Here are four distinct phenomena[2] which need explanation. To solve the problem offered, plates should be exposed when saturated with a solution of potassium nitrite as before, when it will be found that the phenomena are absent, a reversal being almost impossible to obtain unless the length of exposure be such as to thoroughly oxidize the nitrite at the expense of gelatine. For ordinary purposes it may be said that a reversal is non-existent under these conditions.

"If a plate be exposed in benzene, however (a liquid which does not permeate through gelatine), the phenomena are still existent. If a plate be exposed to such an extent that there is a marked image apparent before development, and be then immersed in water, it will be found that when the image appears the gelatine refuses to swell to the same extent that it does when the light has not acted. Taking these two experiments together, it is evident that the gelatine has played some part with the silver bromide. It may therefore be presumed that the three last phenomena are due,

[1] [Hydrogen peroxide.]

[2] Mr. C. Bennett described these phenomena in the *British Journal of Photography* in 1878.

the 1st to the oxidation of the surface-particles of the bromide and a consequent change in color, the 2nd to the change in color of these particles permitting the colored rays to which it is sensitive to strike a deeper layer, and the 3rd to the oxidation of this layer at the expense of the gelatine. The 3rd and 4th phenomena are so unimportant that they are scarcely worth investigating. The presence of organic matter is evidently necessary for their appearance; at least I have never been able to obtain them with collodion films not containing a preservative.

"As before, the experiment of saturating one of these gelatine films with bichromate of potash shows that the reversing action is very much increased by the presence of the oxidizing agent. Mr. Bolas[1] has recently described a plan of producing reversed negatives by allowing the bichromate to dry in the film, which is a practical application of this reversing action of light in the presence of an oxidizing agent.

"A convenient method of showing these phenomena on the same plate is to use a screen containing squares of graduated opacity, as suggested by the editor of the *Photographic News* or such as the sensitometer prepared by Mr. Warnerke, and procurable at most photographic warehouses.

"Having treated of these reversals of the image in a general way, it now remains to show which radiations are effective in producing them. For testing this, spectro-photography was resorted to, a special dark slide having been constructed capable of holding a cell which would contain the plate, and be immersed in a liquid of any gas or vapor whose action it might be desired to test. Three flint-glass prisms were used, and a lens to the camera of about 2 feet equivalent focus, the collimating lens being a duplicate of it. The time of exposure was, as a rule, three minutes to the sunlight or to that of the electric arc, care being taken in the latter case that an image of the positive pole fell on the slit so as to give a continuous spectrum. The action of potassium iodide on silver bromide will first be described.

[1] Photographic Journal, May (1880).

"A plate was exposed after being sensitized, and after washing was immersed in a cell containing a 1 percent solution of potassium iodide and exposed to the spectrum. The result is shown in Plate V,[1] Fig. 1; the same rays which cause an image to be formed in the usual manner likewise caused a reversal (dotted curve, Fig. 1).

" A plate similarly prepared was exposed in a 1 percent solution of potassium bromide for the same length of time, with the result that a reversal was obtained in the blue and likewise in the red, but much less marked in the latter. These two experiments tend to prove that, in reality, it is the bromide that is acted upon to some extent, and the effect is not entirely due to the silver salt. This was particularly manifest in the case of the iodide and bromide slightly acidified with a mineral acid, and was much less marked when the solution was alkaline—in the latter case, the reversal taking place in the blue, and not in the red, regions of the spectrum.

"To see if the silver salt had any marked effect on the rapidity of oxidation, a silver iodide plate was washed, given the same preliminary exposure, and then placed in the spectrophotographic apparatus without any surrounding fluid. A reversal was obtained in the blue, but not to anything like such an extent as when placed in soluble iodides or bromides. The reversal, therefore, when the plate is exposed in the latter, is partially due to the action of radiation on the bromide, and partly to that exerted on the silver salt itself.

"A silver iodide plate, treated as before, was next exposed in a weak solution of potassium bichromate, when there was a strong reversal in the red, and no action whatever in the blue. Permanganate of potash was next substituted for the bichromate, and the same reversing action was found, with the addition of a negative image in the blue.

"With hydroxyl the same phenomena were observed as with the permanganate, the reversal taking place a little further into the green. Studying the absorption due to these

[1] [The figures referred to in the text are not reproduced in this paper.]

three oxidizing agents it would appear that the reversing action *is due to the action of light on the salt of silver, which is changed by the preliminary exposure to light, and not to the action of light on the medium in which the plates are placed.*

"With mineral acids a reversal was always obtained in the red and in the blue, a portion of the spectrum in the green and yellow remaining unreversed. Now the action of these acids is not a strictly oxidizing action, but is probably a removal of the loose atoms of the silver which goes to form the subiodide, and leaving silver iodide behind as the result of the action. The result of the action of acids do not, therefore, vitiate the above deduction. A plate exposed in benzene or in nitrite of potash showed no reversal even with a very prolonged exposure. It should be remarked that the action of permanganate and bichromate of potash when very feeble is sometimes to give feeble negative images in the red and blue in lieu of positive images; also positive images in the blue, and feeble negative images in the red. But this is to be accounted for by the fact that the dilution of these oxidizing agents is so extreme that the reducing action on the unaltered sensitive salt is far greater than the rapidity of the oxidation.[1]

"Ordinary bromide of silver in collodion or gelatine may be taken as giving almost identical results under the influence of a soluble bromide.[2] Now ordinary bromide is sensitive as far as B (see dotted curve, Pl. VI, Fig. 7), and it might be presumed that this sensitiveness to the rays of lower refrangibility would cause a modification in the action of the soluble bromide. A reference to Figures 7 and 8 will show that this is the case, but at the same time the features which are so marked with the action of bromide on silver

[1] There is one singular fact to be noted in this, and which I propose to treat of in another contribution, *viz.*, that the iodide of silver, when given a preliminary exposure, is sensitive in a region of the spectrum lying between a point near D and one near A. This phenomenon has been described before and not explained, though experiments show that the explanation is easy.

[2] As before explained, it is useless to expose such plates in a solution of soluble iodine, since silver iodide is immediately formed.

iodide are present. Fig. 7 is the curves due to silver bromide in collodion which has received a preliminary exposure and was then exposed in a 5 percent solution of acid potassium bromide. It will be seen that the curves in Figs. 7 and 2 are similar, showing that the principal action is due to light acting on the soluble bromide in the presence of an acid. Fig. 8 is a similar plate exposed in an alkaline solution of KBr, in which there is a modification of the curve. The last loop is probably due to the silver subbromide itself, since the oxidation of this salt by oxidizing agents occupies approximately the same position (see Fig. 10).

"Fig. 9 shows the effect of permanganate of potash; and when it is compared with Fig. 10, which is the curve due to oxidation by bichromate of potash, it will be manifest that the chief oxidizing action lies in the red and ultra red of the spectrum.

"Fig. 11 also shows the effect of bichromate of potash on silver bromide given a preliminary exposure, the plate in this case being a gelatine plate. It will be seen that the bichromate totally arrests all action in the blue, while it rapidly causes a reversal in the red.

"Fig. 12 shows the effect of mineral acids on silver bromide, by which it will be seen that a maximum of reversal takes place in the red and in the blue. As before stated in regard to the iodide, the action of these acids can scarcely be regarded as an action of oxidation.

"Fig. 13 shows the phenomena due to over-exposure of silver bromide, by which it will be seen that reversal takes place in the blue and not in the red. Comparing this with Figs. 7, 11, and 12, the effect of extraneous matter in causing a reversal is very marked.

"Collodion plates exposed in benzene, or in aqueous solutions of pyrogallic acid, potassium nitrite, and sodium sulphite gave no reversal whatever.

"Gelatine plates exposed in benzene gave the phenomena shown in Fig. 13, while with the other media no reversal at all was obtained.

"The explanation of the apparent contradiction shown by the behavior of a gelatine plate exposed in benzene has already been given.

"The action of many other liquids and gases[1] have likewise been tried, but it was thought that the examples given sufficed, since they all pointed to the same conclusions, which may be summarized as follows:

"1st. The reversal of an image is due, in the majority of cases, to the oxidation of the subsalt of silver which is formed by the first impact of light on the exposed salt of silver.

"2nd. The oxidation is due to the action of light, the rays of lower refrangibility being the most powerful accelerators of oxidation.

"3rd. Reversal of an image may be due to the presence of any haloid of an alkali, the reversal in this case being partly due to the tendency to oxidation of the subsalt of silver.

"4th. The presence of a mineral acid tends powerfully to cause a reversal."

More or less in line with this are the experiments of Schloemann,[2] who found that "the nitrous fumes from the action of nitric acid on copper turnings produce a solarizing action on ordinary dry plates in a relatively short time. If the gases are prepared by igniting lead nitrate, the reaction is less violent; with short exposures one gets a *normal* image, with longer exposures a solarized one." Since it is not quite clear whether the effective agent is nitric oxide or nitrogen peroxide or both, it is hardly safe to base any conclusions on Schloemann's experiments.

From Eder's Handbuch I quote the following passages:[3]

"If a silver bromide gelatine plate is exposed to light by increasing stages, it acquires to a greater and greater extent the property of blackening in the developer. If the ex-

[1] Ozone was most marked in its oxidizing properties, and gave a curve very similar to Fig. 12, both with the iodide and bromide of silver.

[2] Zeit. wiss. Photographie, 5, 187 (1907).

[3] Eder. Handbuch der Photographie, 5th Ed., 3, I, 111 (1902).

posure is continued longer, the silver bromide plate gets into a state in which there is no increased blackening when developed. With a still longer exposure the photographic plate gradually loses the power of developing, the degree of blackening on development being less than with other silver bromide plates which have been exposed for a lesser length of time. This phenomenon is called solarization. It occurs when very long exposures in the camera are made in an intense light. The brightest portions then develop less black than the dark ones and we get a more or less complete positive direct instead of a negative.

"With an ordinary camera and a lens with a small stop, it is easy to show the phenomenon of solarization by photographing the sun's image direct on a silver bromide gelatine plate, giving an exposure of several seconds, and developing in the usual way. The sun's image on the plate is much more transparent than the sky and the halo[1] round the sun; in other words, we have a positive. When making contact copies on silver bromide gelatine in a printing frame either by daylight or lamplight it is easy to obtain solarized prints if the exposure is sufficiently long.

"When taking interiors against the light, the windows often show solarization effects, coming out less black on development than the adjacent portions (not counting the halo which is often much darker). If such plates are developed with a strong developer, the solarization is very evident. The solarization and also the blurring halos can be reduced to a minimum by under-developing, rinsing off the developer thoroughly, painting the high lights with a potassium bromide solution (1 : 10), letting it dry on a bit, and then developing the plate completely.

"If an emulsion plate has first been exposed to a weak diffused light, a much shorter exposure is then sufficient to solarize it than would have been the case if the plate had not been light-struck. Under some conditions a previously

[1] Due to irradiation.

lighted plate will show distinct signs of solarization with only ten seconds' exposure' to lamplight.

"Solarization phenomena also occur if a normally exposed plate is developed in the light. Silver bromide gelatine plates which have been stained with cyanine (made sensitive for orange), showed marked solarization effects if, during the development and before the picture is entirely out, the plate is exposed for several minutes to a powerful red or yellow light. This inversion of the image is more marked if eight drops of potassium iodide solution are added to the emulsion just before it is poured.[1]

"Waterhouse[2] found that silver bromide gelatine plates which are colored with blue dyes, are in general less liable to solarization than undyed plates or plates dyed yellow.[3]

"The solarization process is to be considered as an oxidation phenomenon, and we assume that with short exposures some of the normal silver bromide is changed into a subbromide, Ag_mBr_n (where n is smaller than m), this subbromide being more readily reduced by the developer than is the normal salt. On further illumination, especially in presence of oxidizing agents, the subbromide takes up oxygen and forms an oxybromide of the general type $Ag_mBr_nO_x$, in which the silver molecule is saturated again and therefore less readily reducible. The consequence of this is that an over-illuminated silver bromide is less readily blackened than one that has received a moderate exposure. This theory was put forward by Abney and further extended by Luggin.[4]

"According to R. E. Liesegang[5] solarized dry plates show a whitish fog on the glass side of the over-exposed portions and he explains this by assuming that the places,

[1] Schumann: Eder's Jahrbuch der Photographie, 12, 391 (1898).

[2] Eder's Jahrbuch der Photographie, 13, 489 (1899).

[3] This cannot be true in general and must depend primarily on whether the dye acts as a sensitizer or as a color screen, and on how concentrated it is.—EDER.

[4] Eder's Jahrbuch der Photographie, 12, 155 (1898).

[5] Ibid., 11, 384 (1897).

where the action of light has been most intense, have become less permeable to the solutions. For this reason he believes that the developer reaches these portions less completely and that they therefore come out thinner.

"As has previously been mentioned,[1] we assume that the silver bromide grain in a ripened emulsion consists of a complex of innumerable silver bromide molecules and we assume that the light acts first only on the surface of the grain. In the case of solarization the "solarized" silver bromide is therefore formed first at the surface of the grains and the production of it in the interior takes place but slowly. A careful examination of a solarized, developed and fixed silver bromide diapositive shows that the transparent portions are not clear glass. Although very transparent, they are nevertheless thickly covered with reduced particles of silver.

"Abney's microscopical measurements showed that the diameter of the solarized particles is smaller than that of normally developed silver grains.[2] One also finds on the surface of the film more of the fine particles than in the deeper portions. This is in favor of the view that solarization occurs chiefly at the surface of the silver bromide where the action of the light is the most intense (in consequence of the oxidizing action).

"With short exposures there is no solarization. In general, the less sensitive the plate, the longer one must expose it before solarization occurs. In round numbers one must expose several thousand times.[3]

"As a rule gelatine plates solarize much more rapidly than collodion dry plates containing preservatives, the difference probably being due to the much greater light-sensitiveness of the gelatine plates. Gelatine plates containing

[1] Eder's Handbuch der Photographie, 5th Ed., 3 I, 101 (1902).

[2] Eder's Jahrbuch der Photographie, 12, 393 (1898).

[3] Eighteen thousand times according to Kogelmann, Eder's Jahrbuch der Photographie, 8, 379 (1894), (10,000 times on an average), as long as is necessary to produce a negative if one is to get a fairly complete solarization. This figure, however, is not constant for all kinds of plates.

both silver bromide and silver iodide solarize somewhat less readily than pure silver bromide gelatine plates.

"The development is not without effect on the phenomenon of solarization. The stronger the developer and the longer one develops, the more readily the plate solarizes. In many cases it is a question of the developer whether the plate solarizes or not. With very dilute developers solarization phenomena are much less frequent than with the 'rapid' developers. An oxalate developer containing a good deal of potassium bromide eliminates the solarization phenomena to a greater extent than the same developer without restrainer. On the other hand, addition of sodium hyposulphite to the ferrous oxalate developer increases the solarization effect with over-exposed silver bromide gelatine plates; the solarized, very transparent, portions of such plates have a different color (reddish) from the non-solarized (blackish) portions. [Eder].

"Metol with an excess of ammonia, or amidol with ammonia, are apt to give inversions analogous to solarization with silver bromde gelatine.[1] A similar effect is obtained with a dilute metol developer containing a good deal of alkali and some thiocarbamide[2] or with an eikonogen developer containing thiocarbamide, allyl thiocarbamide, or especially still better phenyl thiocarbamide. In fact, Waterhouse made this a method of preparing positives directly.

"Starting with an over-exposed silver bromide gelatine plate, which would show marked solarization phenomena when developed in the ordinary way, a normal development can be obtained by treating the plate for fifteen minutes with a solution of 100 cc. water, 3 cc. sodium hyposulphite solution (1 : 20) and 3 cc dilute sulphuric acid (3 : 100), washing, and then developing.[3] The solarized silver bromide is presumably converted into the orthodox developable silver bromide. The result is very uncertain.

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[1] Kogelmann: Eder's Jahrbuch der Photographie, 13, 379 (1899).
[2] Waterhouse: Ibid., 9, 405 (1895).
[3] Kogelmann: Ibid., 9, 419 (1895).

"Solarization phenomena occur also when the silver bromide image is developed physically, in fact even when developed after being fixed as Sterry[1] has shown."

Sterry considers that there are two latent images, one organic and the other inorganic; and that these behave very differently under certain circumstances.[2]

"Soon after the introduction of the collodion process it was noticed that two distinct latent images were impressed upon a sensitive film at the same time by the action of light, but that which is found to remain after fixing the plate has received comparatively little attention.

"The late Mr. R. Carey Lea, Captain Abney and Dr. R. E. Liesegang have dealt with the subject; still, probably owing to physical development being so largely superseded by the introduction of the gelatine plate, it now seeems to be almost forgotten.

"The late Professor Hardwich[3] says: 'The formation of the invisible image is universally allowed to be a molecular and not a chemical change," and in endeavoring to meet some objection brought against this theory, thus describes development after fixing (p. 42).'

"Mr. Young, of Manchester, was the first to show that if an exposed plate be immersed in a solution of hyposulphite of soda, until the yellow iodide is dissolved, a picture will still appear on applying the usual developing mixture." In explaining this phenomenon he says: "Pure iodide of silver is molecularly modified by the camera image, but its properties as regards the action of hyposulphite of soda are unaffected thereby; upon a plate so constituted no image could be developed after fixing. The sensitive surface of the collodion photograph is never, however, an absolutely pure iodide of silver, and sometimes very far from being so. It contains traces of an organic compound of silver in the wet collodion process and more appreciable quantities of the

[1] Eder's Jahrbuch der Photographie, **13**, 289 (1899).
[2] Sterry: Phot. Jour., **22**, 264 (1898).
[3] Phot. Chem., 6 ed., p. 36.

same in the dry processes. Now with a compound film of this kind it may be supposed that while the iodide of silver undergoes its peculiar change in the camera, the organic combination of silver likewise changes, but in a different manner. Without altering in appearance it gradually loses its solubility in fixing agents, so that when the hyposulphite of soda is applied, its removal is not effected.

"Professor Hardwich further concluded that there was a catalytic action exerted upon the organic salt of silver by the actinically excited iodide of silver. This, however, does not at all seem to be necessary, because when gelatine is sensitized with nitrate of silver, development will take place after fixing, with suitable but much longer exposures.

"The molecular theory has recently been enforced by Messrs. Hurter and Driffield,[1] and though the experiments to be described are apparently opposed to that theory, because they indicate that there is some breaking up of the haloid salts of silver at a very early stage of the light action, they nevertheless really uphold it, by showing that the liberation of the halogen is antagonistic to development, not only by its detrimental action upon the remaining haloid salt, but also by its separation and partial loss before development.

"While searching for evidence of liberated bromine by the action of light alone upon gelatino-bromide films, various means were taken to intensify as much as possible the visible coloration by sunlight, which had been supposed to be entirely reduced from the bromide, and consequently evidence of bromine given off. Had the intensification been readily accomplished, it was expected to be able to prove that the action began even with the small light values used for ordinary exposures, because it had previously been found, that if part of a plate was given an exposure sufficient to secure about the highest possible density upon development, and was then exposed to diffused light with the other half,

[1] Phot. Jour., 22, 145 (1898).

that which had received the small initial exposure was the first to darken visibly, thus showing that the reduction had commenced though too small in amount to be visible. Upon attempting to intensify with mercury and ammonia the only result was to change the blue-gray color to brown, and upon using a physical developer as intensifier, no better result was obtained, because at the same time it acted as a developer, giving density to the latent image remaining after fixing, and did not follow the usual rule found for the correct period of either fast or slow plates, during which intensification is proportional to the silver visually found in the developed film.

"From this it was evident that the visible color was not an indication of liberated bromine solely, but probably included and was perhaps mainly composed of an organic silver stain.

"That the coloration is due to silver may be shown by making it into bromide, when the whole is readily dissolved in sodium thiosulphate leaving perfectly clear gelatine.

The latent image remaining after fixing

"Every gelatine plate so far tried—pure bromide or chloride, bromo-chloride, or bromo-iodide—has with suitable exposures given a latent image which, after fixing in sodium thiosulphate, washing and drying, is permanent in daylight, and yet may be developed at any time by means of a physical developer. One that does not necessitate very careful washing is of course desirable, and the intensifier described by Mr. J. B. B. Wellington[1] having proved the most satisfactory has been adopted for all the requirements. Hydroquinone used with acid, as recommended by Dr. R. A. Liesegang, was found to be very slow in action and failed to give sufficient density readily.

"The deposit of silver has far more the character of wet collodion than a gelatine film, with a tendency to a pur-

[1] Brit. Jour. Alm., 1889, 575.

ple-brown tint by transmitted light, especially when chloride is present, thus differing from the simple sensitization of gelatine by the addition of silver nitrate, in which case the deposit is of the transparent ruby color obtained by the direct action of light. If, however, an unexposed bromide plate is fixed, and carefully washed and then sensitized with silver nitrate, the deposit is not nearly so transparent.

"It has been suggested by Dr. Liesegang that the image remaining after fixing is due to the silver reduced by the light, but as it will be shown that this latent image is capable of reversal before the reduction by light alone has reached a maximum, it hardly can be the sole cause. Seeing that chloride of silver is readily soluble in gelatino-nitrate of silver, and bromide also to some extent, it would seem more probable that it is partly due to the silver haloid being either dissolved in or perhaps even chemically combined with the gelatine; therefore following Prof. Hardwich's explanation, it will be called the organic latent image in contradistinction to that impressed upon the visible haloid particles, and which will be described as the inorganic image.

"By giving a plate a series of exposures and comparing portions developed before and after fixing, it is found that usually no agreement beyond a single tone can be obtained (Table I).

TABLE I

Exposure	Density		
	A Inorganic latent image. Development before fixing	B Organic latent image. Development after fixing	A–B Difference
1	1.53	0.7	+0.83
4	1.71	1.0	+0.71
16	1.82	1.35	+0.47
64	1.87	1.7	+0.17
256	1.57	1.75	—0.18
1024	1.37	1.64	—0.27

"If the ordinary development is made to agree with either a high or low tone of the organic image, the scale in either case rapidly separates.

"If a number of plates are exposed, fixed and developed together, the organic image upon each is found to have points of agreement not found in developed inorganic images, while at the same time some relationship is maintained between the two latent images, organic and inorganic.

"The most striking results found are:

"1. That the highest density is with an occasional exception obtained with the slowest plate.

"2. The highest density is so very different with slow and rapid plates that it is necessary to divide them into at least two classes, say above and below H and D,[1] speed 10.

"3. That reversal usually takes place at or near the same exposure, not differing more than one exposure, and this in favor of an earlier reversal with the most rapid plate.

"4. Reversal is always reached earliest by the inorganic image and re-reversal by the organic.

"5. Giving much smaller exposures so as to obtain commencement of visible reduction it is found that there is very little difference in the plates (in either class taken separately), the higher speeds showing about one exposure before the slow, from which it would seem that whatever means are used to produce rapidity in gelatine emulsions, the sensitive organic compound, in this respect, remains far more nearly constant than the inorganic.

"6. The organic image is developed throughout the film, often leaving the surface as bright as the glass, while the developed inorganic image is evidently largely upon the surface.

"7. The inorganic latent image is not completely insoluble in sodium thiosulphate as supposed by Prof. Hardwich, but it is, however, far less soluble than the inorganic, thus giving the opportunity of isolating and developing it. Pro-

[1] [Hurter and Driffield.]

longed immersion appears to remove it entirely, though very slowly, after the first half hour. The reduction is found to follow the usual rule, entirely altering the gradation and giving an appearance of under-exposure.

"After fixing, the length of time required for washing is at least fifteen minutes, otherwise with some plates there will be a tendency to deep red fog. The more completely the washing is performed the quicker and better will be the development.

"It will be well to note at once, where accuracy of comparison is desired, this partial removal of the latent image and alteration of the scale of gradation during fixing, necessitates each experiment being made complete in itself. After various trials the time of fixing was settled at eight minutes, with thirty minutes' washing in running water.

"While it is evident that after fixing it is the organic image alone that is dealt with, it is not so clear that the reduction of silver by ordinary development is due to the action of light upon the haloid salt alone. That the organic image is in some way connected with the inorganic seems highly probable, seeing that there is an apparent inverse relationship between the density obtainable from the organic image and the speed of the plate to ordinary development, and also because the form of the original bromide particles is reproduced with the physical development of the organic image.

"After development of the inorganic, no trace of the organic image can be found. The physical developer does not then add the densities due to the organic image, but, as previously stated, a proportional increase of the developed densities, and largely upon the surface. This is no proof whatever that the organic image is either used or destroyed in the development of the inorganic, because it is possible greatly to retard the development of the inorganic image while leaving the other practically uninjured. It would seem, however, that little or no building up of the organic image can take place in the presence of the silver ordinarily

reduced by development. If the development is stopped with the merest trace of image, and is followed by the intensifier, the organic image may be sometimes traced.

Speed relationship

"The following table gives the comparative speed relationship of a few different plates (Table II):

TABLE II

Comparative Speed of Organic and Inorganic Images, Hurter and Driffield Speed Nos.

Inorganic	Organic	Development factor	Inorganic	Organic	Development factor
1.6	0.7	1.2	34	6.0	0.65
4	1.0	1.3	41	8.0	0.50
4	1.6	0.9	75	11.0	0.45
5.5	2.0	1.25	87	11.0	0.43
17	2.0	1.00	115	28.0	0.30

"While the H and D speed numbers of these plates vary from 1.6 to 115, a ratio of 1 to 72, the speed numbers of the organic image taken in the same manner range from 0.7 to 28, a ratio of 1 to 40, still it must not be considered that the speed varies so much in reality, because, as Messrs. Hurter and Driffield have pointed out, the actual speed of the plate is indicated by the point of double flexure in the characteristic curve, and the flatness of the curves obtained with the high-speed plates is really misleading, precisely as they have shown is the case when a plate is too thinly coated.

"The point of double flexure is difficult to ascertain accurately, but the greatest apparent difference is not more than 1 to 8, or one-sixth of the variation in speed of the inorganic latent image.

"In a very large number of cases the relative speed of plates to development may be correctly estimated from the simple comparison of the densities obtained from the physical development of the organic image in equal times, and so far the method has been found to fail only when the color of

the original plate differs greatly, so that the proportions of chloride, bromide and iodide apparently affect the results obtained, the chloride having by far the greatest influence. Indeed, were it not for the complication due to the mixed haloids, the speed of plates could probably be fairly well estimated from standard plates, by simple comparison of the reflections of a gas flame from the surfaces. Many successful trials have been made in this way, only failing as in the previous case when the color differed greatly.

"A sa general rule when two plates are compared together by means of the physically developed organic image, the slowest will give the greatest density at three points: 1. Between correct exposure and reversal. 2. Between reversal and re-reversal. 3. Density of re-reversal. Table III:

TABLE III

Exposure	Density			Exposure	Density		
	A	B	C		A	B	C
	Speed 17	41	87		Speed 17	41	87
1	1.24	0.73	0.63	158	1.51	0.71	0.58
3.55	1.46	0.79	0.68	562	1.56	0.75	0.63
12.6	1.60	0.77	0.59	1970	1.72	0.88	0.72
44.7	1.55	0.70	0.57	—	—	—	—

"The exposures were made at one time in diffused daylight under a negative constructed with layers of celluloid of equal density, giving approximately the exposures shown.

"With the organic latent image the period of reversal is very short indeed, and a rapid, and compared with the inorganic, intense re-reversal sets in quickly, 30 seconds to diffused daylight being sufficient to show the commencement, whereas using the most rapid plate, eight days has been the shortest time so far found for the re-reversal of the inorganic image, and a slow plate had not nearly completed reversal at the end of two months' exposure.

"With plates below 30 H and D, exposures may be obtained in the camera and lantern slides made, and under some circumstances might prove useful, owing to the almost complete absence of halation. Above this speed, the density obtained is so small that the plates are not readily available practically.

"Before development the films are perfectly transparent and colorless, while all needed density can usually be obtained in from 5 to 10 minutes.

"As to the practical value of the organic image probably not much can be said. The advantage of working in white light is not sufficient to counterbalance the disadvantages of the longer exposures required, and the tendency of the strong developer to bring out the slightest deterioration in the film. There is, however, one point worth notice. The great density readily obtained without halation when chloride is present in quantity and the exceedingly abrupt commencement of the curve, especially when reduced in the fixing bath, permits of great contrasts being obtained and may possibly prove of service in process work.

"In a former paper[1] the results were given of a number of experiments specially arranged to ascertain the effects of moisture and free bromine, as likely to be disturbing causes in the estimation of the speed of plates and to throw light upon the differences mentioned. The following conclusions were given (p. 127):

"A. Moisture increases the reduction of silver by development in a given time during the correct, over-exposure and reversal periods.

"B. Concurrent with the formation of the developable condition by the action of light, a constantly increasing counter-action is set up by the halogen liberated.

A. Moisture. Effect upon Organic and Inorganic Images

"A plate is invariably in its most rapid condition when thoroughly dried, the speed rapidly decreasing when moistened.

[1] Phot. Jour., 19, 118.

"At the same time moisture increases the amount of silver reduced in a given time as indicated by the increased development factor, and thus is in accord with the usual rule, the slower the plate the quicker the development.

"It is when the greatest density and reversal period is studied that the effects of moisture become more evident. The intimate relationship between the light and the amount of silver reduced which is found during the correct exposure period, no longer exists. Dealing still with the inorganic image, the slightly increased reduction found throughout the scale during the correct period rapidly increases, delaying reversal, and causing the fall during that period to be far less rapid.

"It is also noticeable that the greatest density attained is far higher in the moist than in the dry plate.

"Turning now to the organic latent image, it is found that moisture has a similar but far less marked effect.

"With some plates little or no difference is found until reversal is approached, but, as before, this seems to be invariably delayed by the moisture (Table V).

TABLE V

Exposure	Density Organic latent image		
	Dry plate	Plate moistened before exposure	Difference
1	0.40	0.45	0.05
8	0.66	0.72	0.06
64	1.12	1.22	0.10
512	1.03	1.46	0.43

"The effect of moisture thus appears to be a very general one, for it has already been shown to apply to the visible reduction by light alone.[1]

[1] Phot. Ann., 1894, 293.

B. Bromine. Effect upon Organic and Inorganic Images

"The second conclusion was that concurrent with the formation of the developable condition of the action of light, a constantly increasing counter-action is set up by the halogen liberated.

"This counter-action was supposed to be directly caused by the action of the released halogen upon the latent image, and though it could not be actually detected, appeared to be the main cause of the anomalous results obtained under different conditions of exposure.

"If a pure chloride or chloro-bromide plate is taken, there is not any difficulty in showing visible reduction of silver by light alone with exposures far short of reversal with the organic image and a little short with the inorganic, and as it is these slow plates which have always been found to exhibit the most striking differences under varied conditions of exposure, support is given to the view that such variations even with bromide plates are in some way connected with the release of the halogen.

"Further investigation, using the organic as well as the inorganic latent images, throws more light upon the subject, the reversal period being especially helpful.

"The bromine known to be liberated with high exposures cannot be considered simply as the direct cause of reversal, nor does it really destroy the latent image, though for practical purposes that appears to be the case, but its real action is to retard development, which will take place if sufficient time is given.

"It was before shown that the application of a solution of bromine to a plate before and after exposure produced similar results, development being retarded in proportion to the strength and time of application. The effect is also found to be much greater than after exposure, and always (except when the quantity is very small) giving the appearance of under-exposure.

"With the organic image similar results are found, but there appears to be much more difference in the behavior

of fast and slow plates; all bear far stronger solutions, especially the rapid, ten times the strength for the same length of time being sometimes required to obtain an equal reduction. When this is the case there is not any difficulty in practically discharging the inorganic image by means of the bromine and yet leave the organic image capable of development. Generally therefore it would seem that the organic image is far more stable than the inorganic. In *Brit. Journ.*, December 22, 1865, the late Mr. R. Carey Lea noticed its extraordinary persistency.

"There is, however, one marked peculiarity: the organic latent image of all plates tried has been seen to have a short and sharp reversal period followed by re-reversal, and the effect of bromine when applied of suitable strength is to remove the reversal altogether, making one unbroken curve up to what was before the re-reversal period.

"It is then found that the curves of the organic and inorganic images, with some plates, cross one another, giving a positive and negative from the same exposures (Table VI).

TABLE VI

Exposure	A Inorganic latent image	B Organic latent image	C Organic latent image Bromine before development
1	2.15	0.75	0.28
3.55	2.14	0.83	0.35
12.6	2.05	0.96	0.45
44.47	1.51	1.03	0.64
158	1.05	0.97	0.80
562	0.76	0.94	0.98
1970	0.49	0.97	1.04

"The organic gives the negative, and the inorganic the positive, by means of ordinary reversal.

"Whether applied before or after exposure the effect of bromine upon the organic image is always to delay reversal, and this rule is found to include the inorganic image also. Being the most important, proof only of this result when applied after exposure will be given.

"The first effect found when the time and quantity is small is delay in development, but if sufficient time is given to obtain the same development factor the plate is apparently increased in speed and that instead of a falling off in the density of the highest exposures, there is a decided increase. If a longer time is given this latter peculiarity is still more strongly marked, while at the same time the lower tones fall off and there is a decrease in the speed of the plate indicated.

"The action of bromine is thus seen to be exactly opposite under different conditions (Table VII).

TABLE VII

Exposures	A Ordinary development	B Bromine, 2 minutes before development	C Bromine, 8 minutes before development
1	0.10	0.14	0.05
4	0.32	0.40	0.33
16	0.66	0.87	0.97
64	1.13	1.32	1.66
256	1.57	1.77	2.36
1024	1.97	2.28	3.36

"From these results it is clear that if the time of application of the bromine is adjusted half-way between the curves *A* and *B* there should be a considerable prolongation of the correct period of the plate (Table VIII shows that this is the case).

TABLE VIII

Exposures	A Front of plate	B Back of plate	C Front of plate Bromine before development	D Back of plate Bromine before development
1	1.46	1.05	0.44	0.42
8	1.96	1.74	0.92	0.88
64	2.41	2.44	1.50	1.41
512	2.46	2.77	1.87	1.78
4096	2.04	2.50	2.29	2.26

"The curves *A* and *B* are the same exposures and development, the only difference being that *A* was made upon the face of the plate and *B* upon the back. *A* gives the plate as more rapid for the correct period and therefore requiring less exposure for ordinary work, but the density reached is less than *B*, reversal also is earlier and more rapid.

"Other portions of the same plate (*C* and *D*) were also exposed at the same time back and front, and were placed in one percent of saturated solution of bromine for eight minutes and then washed.

"Development was greatly retarded, but the exposures are now shown to be practically identical for both back and front of plate, and the correct period has been greatly extended, giving almost a true representation of light intensities from 1 to 4,000.

"It was shown in the previous paper that the difference found with exposures given for a short time with strong light and longer time with a weak light, were not due to any differences in the lights themselves, for when the duration of exposure was made the same and the lights placed at proportionate distances the results were identical. That this is accounted for by the action of bromine is further proved by the last experiment, in which the bromine has been made to play a double part, preventing the surface from being developed (a coating of bromide covering the whole plate before fixing), thus giving time for the low tones to be developed at the back of the plate, and at the same time bringing the reversed portions again into a developable condition. The whole is of course an artificial arrangement but based upon what appears to be the reversal of the ordinary conditions of action within the film.

"It has long been known that bromine absorbents delay reversal, but it does not appear to have been suggested that they do so by returning the bromine.

"The action of the moistened plate would seem to be due to its great power of temporarily holding the bromine, for it has been noticed that the visible reduction is much

greater than with the dry plate, and consequently much more bromine must be given off.

Summarizing briefly the results obtained it would seem

"1. The organic image may be due to three different causes:

"A. An organic silver compound (Hardwich). B. Silver haloid dissolved in, or combined with the gelatine. C. Intensification of the silver reduced by the light alone (Dr. Liesegang).

"2. The perfectly developable condition of the inorganic image is probably a molecular change only.

"3. With different plates, as also under varied conditions of exposure, more or less molecules of silver haloid are broken up and the halogen liberated, causing a reduction in the development.

"4. Reversal is mainly due to two causes: 1. Directly, by loss of the halogen. 2. Indirectly, by the injurious effect of the halogen upon the development of the remaining haloid salt.

"5. When the conditions permit of part of the halogen being returned either directly or from the gelatine, development is greater, and the tendency to reversal is delayed."

In an article on the nature of the latent image, Eder[1] comments as follows on the assumptions of Hardwich and of Sterry in regard to the existence of an "organic" image.

"Hardwich based this theory on some badly carried out experiments of his own. He held the erroneous belief that pure silver iodide collodion films lose the latent image when fixed and that an image, which can be developed, remains after fixing, only in films which contain organic substances such as albumen, etc. He therefore considered the organic substances as important constituents of the latent image. As a matter of fact, however, even after fixing there remains on a *pure silver iodide collodion film* a latent image which

[1] Zeit. wiss. Photographie, 3, 331 (1905).

can be developed, so the bottom falls out of Hardwich's proof.

"Sterry made no attempt at a proof and merely assumed that the component of the latent image on silver bromide gelatine, which remained after an initial fixing, must be a decomposition product of silver bromide with gelatine,[1] apparently because he could think of no other explanation for the unexpected behavior of the latent image after fixing. When one reflects that exactly the same phenomenon is shown not only by silver bromide gelatine but by silver bromide collodion even in presence of a concentrated nitric acid or silver nitrate solution, the existence of this hypothetical compound of silver subhalide and organic substance seems very doubtful, and the doubt increases if one studies more closely the behavior of the latent image in silver bromide collodion towards chemicals."

Lüppo-Cramer[2] records the following observation with a silver iodide plate:

"I noticed one surprising occurrence in a solarization experiment with silver iodide gelatine. Under a negative the plates gave a properly exposed image when exposed three seconds in diffused daylight. A plate exposed for six hours under the same negative was developed in the same dish with the plate which had been exposed for three seconds, using amidol-potash. At first the plate seemed not to reduce at all, even when all the details had appeared on the plate with the short exposure. After some time a picture was noticed on the over-exposed plate. It was to be seen, however, only in the *deeper layers* and was a normal diapositive, *i. e.*, not yet solarized. Only after a longer development could anything be seen on the surface. When the plate was fixed, it was clear that there was no image in the *upper layers*. When only a few minutes in the fixing-

[1] Silver nitrate, mixed with gelatine, also gives an image which can be fixed and then developed physically. Sterry: Eder's Jahrbuch der Photographie, 14, 290 (1899).

[2] Eder's Jahrbuch der Photographie, 17, 46 (1903).

bath, the image appeared more powerful by reflected light, evidently because the unreduced silver iodide of the upper layer was removed."

The same author considers that the gelatine is an essential factor in the solarization process, for he says:[1]

"Chemically-pure, dry silver bromide, precipitated in a pulverulent form from aqueous solution and free from a bonding medium, shows no absolutely certain solarization phenomena. On the other hand, the solarization of silver bromide gelatine dry plates can be followed by quantitative analyses. When silver bromide gelatine is given a normal exposure and developed with ferrous oxalate, the reduction to metallic silver is five times as great as when a similar plate is given a moderate solarizing over-exposure (one minute of daylight, for instance). Only after a twenty-minute exposure to direct sunlight,[2] does a silver bromide collodion show solarization effects when developed. Treating with dilute bromine water or with strong nitric acid destroys the solarized image and gives rise to a normal negative on development. Stronger bromine water destroys also this last-mentioned negative image."

This view is disputed by Schaum who obtained quite different results.[3]

"The phenomenon of solarization is often attributed to an action of the binder (hardening). While this is possibly a not unimportant secondary factor with gelatine plates, the actual solarization process must, however, have its cause in some peculiar change in the silver bromide itself, for our films solarize quite distinctly, and a smaller phenomenon has been reported for Daguerreotype plates. Luther did not obtain such an effect with his films. Our solarized films behaved exactly like solarized dry plates. Bathing in ammonium persulphate solution (five percent and twenty-two hours' soaking) destroys solarization completely, so the strips,

[1] Lüppo-Cramer: Ibid., **16**, 481 (1902).

[2] It was proved that bromine was set free.

[3] Schaum: Eder's Jahrbuch der Photographie, **18**, 76 (1904).

which have been exposed the longest to light, become the blackest when developed.

"The action of Röntgen rays on silver bromide, containing no binder, is interesting in some respects. Whether precipitated on glass or on potassium foil, the silver bromide, free from binder, is changed by Röntgen rays into a state in which it can be developed. The Röntgen rays therefore themselves cause a change in the silver bromide quite apart from any fluorescence arising from the supporting plate or the binder, as has sometimes been assumed.[1]

"After an exposure of eighty minutes to the Röntgen rays, we were able to detect a solarization of our silver bromide, free from binder, even though this was not observed by F. Hausmann[2] with dry plates."

In the paper referred to, Miss Hausmann[3] "studied the relation between the amount of silver bromide gelatine when subjected to the action of light in the one case and to the action of Röntgen rays in the other. The silver was determined volumetrically after the plate had been developed, fixed and washed, and the gelatine film then removed and treated with nitric acid. Ferrous oxalate was used as developer and Lumière plates were selected because the unexposed emulsion was least attacked during development. The development lasted five minutes in each case. The illumination was made with a benzene candle at a distance of one meter. By comparison with an amyl acetate lamp the light was expressed in terms of meter-candles. The amount of silver precipitated increased up to an exposure of 180 seconds and decreased for longer exposures. The experimental increase with the time was compared with the change required by the formulas of Bunsen and Roscoe, of Hurter and Driffield, and of Abney. No one of the formulas holds very well. When a Welsbach light was used, the maximum effect was obtained in 10 seconds. As the exposure was in-

[1] Cf. Eder's Handbuch der Photographie, 5th Ed., 3, 69 (1902).

[2] Beiblätter, 27, 359 (1903).

[3] Ibid., 27, 359 (1903).

creased to an hour, there was a rapid decrease in the amount of silver precipitated. With still longer exposure (1–8 hours) the decrease was relatively slight. In daylight and in sunlight the maximum was reached in the first second. With Röntgen rays the effect at first increased rapidly with increasing length of exposure, then at an ever slower rate until a maximum was reached at about 10 minutes; there was, however, no definite decrease on still longer exposure. At the same distance, the action of the normal candle was 33.6 times as great as that of the Röntgen rays when the exposure was ten seconds. For ten minutes' exposure the figure was 22.3 instead of 33.6."

Schaum's experiments on the solarization of pure silver bromide have been confirmed by Weisz,[1] who, however, had difficulty in getting the phenomenon and who says:

"We are therefore only in the position to state the fact that solarization occurs with plates containing no binder. Although it is probable that the best way really to learn something about solarization is by experiments with plates containing no binder and although we have worked hard along this line, we have not yet succeeded in being able to repeat our experiments satisfactorily when using plates containing no binder."

Some very remarkable cases of reversal have been re corded by Goldstein:[2]

"The coloring of alkali salts, which was first obtained with cathode rays, can also be produced by ultra-violet light.[3] Daylight causes the color to disappear. The change produced by ultra-violet light, or by cathode rays (whose action can also be referred back to ultra-violet light[4]) is thus reversed by light of a greater wave-length. The colors which silver salts acquire under the action of light or of cathode

[1] Zeit. phys. Chem., **54**, 351 (1906).

[2] Verh. deutschen phys. Ges., **3**, 182 (1901).

[3] E. Goldstein: Thätigkeitsbericht der Physik. Techn. Reichsanstalt für 1895; Zeit. Instrumentenkunde, **16**, 211 (1896).

[4] E. Goldstein: Sitzungsber. Akad. Wiss. Berlin, **1901**, 227.

rays resemble the colors developed in the alkali salts, and the question at once arises whether these changes may not also be reversed by light or other physical agents.[1] A reversal by action of light is of course only to be expected with such silver salts as are not affected by daylight and are blackened by ultra-violet light or cathode rays. For the sake of convenience we will denote by 'blackening' all darkening of the illuminated silver salts, regardless of whether the actual color is blackish-violet, dark greenish-gray or something else. By 'regeneration' is meant the return to the color characteristic of the unexposed salt.

"First to be described is a type of regeneration which apparently contradicts the previously established limitation of unchangeability in light because it refers to silver bromide and silver chloride, both of which salts blacken in daylight under ordinary circumstances.

"When silver chloride in a sealed tube has been blackened by the action of sunlight, it is well known that the salt takes up the freed chlorine gradually in the dark, becoming white. Previous experiments have shown that, with a continuous illumination in a closed vessel, a state of equilibrium is reached beyond which the blackening does not go. The state of equilibrium is reached when the concentration of the chlorine set free by the intensity of the light in question has reached the corresponding dissociation pressure.

"It appears not to have been observed that under these conditions a reversal of the blackening may take place, running even to complete regeneration. The action in question is particularly easy to obtain with silver bromide. Granular or pulverulent silver bromide is blackened by being allowed to slide many times through a sheaf of powerful cathode rays generated at a very low gas density. The blackened salt is then placed in a vertical half-filled glass tube about 16–18 mm in diameter and exposed to the direct sunlight.

[1] According to Abegg, Wied. Ann., **62**, 433 (1897), silver bromide, which has been made gray by the action of rays, can be changed back into the yellow salt by heat.

At the end of about three-quarters of an hour only the free surface and the illuminated ("front") half of the cylindrical column of salt is black. The back, and especially the whole interior, of the mass is completely regenerated and cannot be distinguished by the eye from freshly prepared salt. If the tube is placed in a diffused light at a bright window instead of in direct sunlight, about two summer days are necessary to regenerate silver bromide while several months are needed for silver chloride. The experiments succeed also with silver bromide or silver chloride preparations which have been blackened by daylight in the open air and not by cathode rays.

"The regeneration in the closed space is due to the fact that the sun acts on the side towards it and gradually works in deeper, setting free bromine and tending to produce the dissociation pressure corresponding to the prevailing intensity of the light. On the less strongly illuminated portions, the back and the inside, the dissociation pressure, corresponding to the chemical equilibrium, is lower. Therefore bromine diffuses from the front to the less strongly illuminated blackened portions combining with them to form regenerated salt. This continues so long as the mean pressure of bromine in the tube exceeds the dissociation of the weakly illuminated portions. The explanation is the same for the case of the regeneration of the salt blackened by the cathode rays. A special case of the action in question is that in a closed tube lighted from above, it is impossible with continuous illumination to blacken both the upper and the under sides of silver bromide simultaneously. What is at the moment the surface is always blackened while the under side loses its color.

"With a continuous illumination in the open air, diffusion and air currents prevent the utilization of the free bromine and there is therefore an increasing blackening and decomposition without regeneration.

"This way of looking at the phenomena is in harmony with the facts that blackened silver bromide is made yellow

again when brought in contact intentionally with free bromine, and that the fresh yellow salt is not blackened at all by direct sunlight provided there is present a sufficient excess of free bromine.

"In a second type of regeneration the relations seem not to be quite so simple. It is interesting because blackened silver bromide, which is usually so stable, can be changed back in a few seconds into the yellow salt. It is best for this purpose to use a silver bromide prepared pretty closely according to the process described by Abegg.[1] Silver chloride is first precipitated from a silver nitrate solution by means of hydrochloric acid; it is dissolved in ammonia, and silver bromide is then precipitated from this solution by means of potassium bromide and nitric acid. The object aimed at by Abegg in this process is to prepare a salt which can be pulverized easily and which will not cake. For the effect which interests us the salt works best when it is not washed until completely pure, but when a trace of a definite impurity, presumably ammonium nitrate, is left in. The salt is then to an extraordinary degree less sensitive to daylight than the ordinary modification of silver bromide. Only after exposure of hours or even days is it darkened as much as the ordinary silver bromide after an exposure of a few seconds. When subjected to cathode rays, however, it rapidly becomes greenish-black. It therefore satisfies pretty completely the condition originally laid down for a regeneration produced by light. An extra advantage is that under the influence of the positive light of the discharge through air at very low pressure the salt also remains yellow even on long exposures.

"In consequence of the trace of the other salt adhering to it, this silver bromide, when heated in a vacuum, gives off a gas whose color and spectrum is that of nitrogen. The necessary heating is produced by the cathode rays which blacken the salt at the same time. If the discharge tube has the form of Fig. 1 for instance, the cathode rays from the aluminum

[1] Wied. Ann., 62, 425 (1897).

disc *K* meet the salt at S and blacken it. The blackened salt is moved, by tipping the tube, into the region of the stratified positive light, corresponding to the discharge through the gasified trace of the other salt; the blackening disappears in a fraction of a minute. Even without a displacement of the salt, the regenerating action of the positive light can be detected by the asymmetric distribution of the color if the salt is scattered all along the tube R. If the vessel is pumped out only to the point at which the cathode rays are still visible with their blue light, the purely optical effect of this light is to blacken the salt not only where the cathode rays strike it at the region S but also at the left end of the tube. To the right of the cathode rays however the salt remains yellow because the blackening due to the blue light is continually compensated by the regenerating action of the positive light.

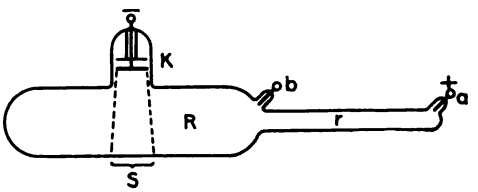

Fig. 1

"If one wishes to make the conditions simpler, it is possible to dispense with the blackening by the cathode rays and to produce both the blackening and the regeneration with the positive light. To do this, the portion of the salt to be examined is brought into the field of the positive light and in the region of the cathode light there is only left a trace of salt from which the cathode rays generate gas, chiefly as a result of heat action. If the gas pressure during the discharge has reached a certain value, very small in itself, but at which the positive discharge no longer fills completely the tube *r* which is about 16 mm. in diameter, we get a light which is dull to the eye but which is apparently rich in ultraviolet rays and which blackens the salt very rapidly (inside of two seconds). Simply by pumping out to the earlier and

smaller gas pressure, the light becomes brighter and the blackened salt changes back again into the yellow salt. In this experiment if one puts in a stop-cock between the tube and a pumped-out vessel, the gas pressure in the tube will rise quickly when the stop-cock is closed and will fall again when connection with the pumped-out vessel is restored by opening the stop-cock. Under these conditions the salt can be repeatedly blackened and decolorized merely as a result of turning the stop-cock.

"Regeneration can also be brought about at constant gas pressure. By closing the stop-cock and allowing the pressure to rise, blackening is produced by the positive light. If the pressure is then kept constant and the salt heated from without by means of a Bunsen burner, the blackening disappears in a few seconds but re-appears again as the salt cools once more. A necessary condition for these changes is always the simultaneous action of the positive light. If one heats or cools without having a current passing at the same time, there is no change in the color. In this experiment the heating by means of the cathode rays can of course be omitted.

"Though the positive discharge passed over the salt in all these experiments, the regeneration is not due to a specific action of the positive discharge on the salt. This follows from the fact that regeneration also occurs when the salt has been blackened in the positive light and is then brought into a part of the tube through which no discharge passes, for instance into *R* while the discharge is made to take place between *a* and *b*.

"I will now record some observations on the behavior of silver iodide.

"When silver iodide is prepared from silver nitrate and an excess of potassium iodide, its yellow color is known to change but little in daylight. According to Stas there is no loss of iodine during this change. Under the influence of the cathode rays the salt becomes dark black and does lose a little iodine. This can be shown by bringing a few pieces

of bright copper foil close to the illuminated silver iodide. At first the copper does not light up in the cathode rays, but in a short time it phosphoresces with an intense fiery-red light. The iodine set free from the silver iodide reacts to form cuprous iodide which phosphoresces with this color.

"If silver iodide is blackened by cathode rays in a sealed tube containing no copper and if this tube is then placed in daylight, after a few days the salt will be found to have bleached to the same whitish-yellow color which fresh silver iodide acquires in daylight. The iodine, which had been previously set free, recombines under the influence of daylight.

"Regeneration takes place in a few seconds if silver iodide, blackened by cathode rays, is brought into the field where the discharge of positive light can pass through the iodine vapor. If the salt is to be regenerated, it must also be heated a little.

"If one starts with yellow silver iodide in the part of the tube through which the positive light passes and if, after the tube is exhausted very thoroughly, a little silver iodide is decomposed by the cathode rays, the silver iodide exposed to the positive light takes on an orange to red color. This is the color which also appears if iodine vaporizes in a closed space near yellow silver iodide. The coloring is due solely to a physical adsorption of the iodine. One special factor comes in, however, in the production of the color by means of the discharge, as can be seen if one spreads the yellow silver iodide over the whole length of a tube like that in Fig. 2. In the middle of the tube the cathode rays, starting from *K*, set free some iodine. In a short time the silver iodide becomes colored a deep orange over the stretch *KA* where it is exposed to the positive light. The salt in the left half of the tube remains unchanged in color and only after a long period of discharge does the left side assume a color which even then is much fainter than that of the right half and which corresponds to the ordinary adsorption.

"If now a part of the highly colored right-half is wrapped in black paper while the rest is exposed to daylight, the orange

color disappears in a short time from the illuminated portion while the shaded portion remains unchanged. It looks therefore as though very refrangible light increases the absorptive power of silver iodide for iodine, while light of greater wave-lengths decreases it. Experiments were made to see whether under similar conditions all substances acquired a strong absorptive power for iodine. This proved not to be the case for barium sulphate. On the other hand, amorphous silicic acid anhydride (from Kahlbaum) becomes active and is colored a beautiful pink when placed in a discharge tube in which silver iodide was placed under the cathode to act as a source of iodine. When brought in contact with iodine in a test-tube, barium sulphate was not colored while silicic acid anhydride became pink. The discharge light therefore seems only to strengthen a previously existing power of absorption, which is weakened by ordinary light."

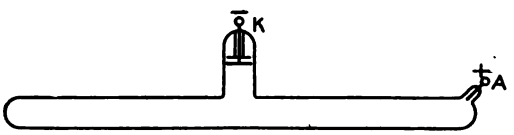

Fig. 2

Coming back to the action of ordinary light, we find that the degree of solarization is not a function of the exposure alone, but depends on the chemical treatment which the plate receives before or during development. Thus Lüppo-Cramer[1] says that "on treating solarized plates with bromine and nitric acid, I obtained a change of the solarized image to a normal image on developing, though curiously enough the image, which was present before development, persisted."

Eder[2] found that washing the plates before development in a bath containing

2 g potassium bichromate,
2 cc nitric acid, sp. gr. 1.4,
100 cc water,

ensured the development of a normal negative even though

[1] Eder's Jahrbuch der Photographie, 16, 54 (1902).
[2] Phot. Correspondenz, 1902, 645, 703.

the exposure had been several million times too long. Weisz[1] found that the solarization was eliminated to the same extent regardless of whether the plate was transferred direct from the chromic acid bath to the developer or whether it was washed for fifteen hours in running water. Of course if the chromic acid solution is too concentrated, the normal latent image is also destroyed, as has been shown by Sheppard and Mees,[2] who say:

"It has frequently been maintained that halogenizing and oxidizing agents do not actually destroy the latent image, but only retard development. Sterry,[3] for example, considered that their effect was to delay what he termed "secondary development," *i. e.*, an assumed intensification of a primarily formed image by silver from neighboring granules. Our experiments with chromic acid subsequent to exposure led to the following conclusions:

Plates were dipped by rotation in CrO_3 solution for a given time, then rinsed by rotation and developed.[4] The plate-curve was distorted at the top, but log i and γ_∞ were unchanged.[5] The velocity constant K of development was diminished, approximately in proportion to the *logarithm* of the strength of the preliminary CrO_3 bath. Prolonged washing never entirely annulled the effect, but it was diminished. The values of K (the velocity of development) decreased with the time of immersion in CrO_3, ultimately reaching a minimum for each concentration, the function of the effect on K being independent of the concentration.

"From these facts we conclude that the CrO_3 is irreversibly absorbed in the film, probably both to the film and to

[1] Zeit. phys. Chem., **54**, 341 (1906).

[2] Proc. Roy. Soc., **78A**, 463 (1906).

[3] J. Sterry: Phot. Jour., **54**, 50 (1904).

[4] For the author's experimental methods, and for the meaning of the symbols log i and γ_∞, etc., see the previous papers. Roy. Soc. Proc., **74**, 447 (1904); **76A**, 217 (1905).

[5] ["i is a characteristic constant of the plate, termed the inertia, and γ is a constant depending upon the development and called the development factor." See Proc. Roy. Soc., **74**, 466 (1904)].

the silver halide, forming with the latter something of the nature of a solid solution. Freshly precipitated AgBr is colored yellow by chromic acid, and the color is not removed by long washing. The retained oxidizer then shows development by oxidizing the developer in the film. This view was further confirmed as follows: Plates were treated, after 'chromating,' with a solution of sodium sulphite, which restored K to its normal value by reducing the chromic acid.

"This 'sulphite reaction' enabled us to decide without doubt that the prolonged action of CrO_3 destroyed the latent image, *i. e.*, both log i and γ_∞ were altered. *After* sulphiting, since K is now restored to its normal value, any change in γ is due to a lessening of the mass of the latent image. The following table exemplifies the results for N/50 CrO_3, with a subsequent bath of N/10 Na_2SO_3, all developed in M/20 quinol for five minutes:

t = time of immersion in CrO_3 in minutes.

	$t=0$.	2.	20.	40.	120.
γ	1.65	1.65	0.77	0.48	0.34
log i	1.25	1.25	1.30	1.50	1.80

"The rate of attack on the latent image was found to increase very rapidly with the concentration of the CrO_3. The phenomena point to a re-oxidation (possibly involving the release of halogen from a combination with gelatin) of a reduction product, the latter being in solid solution in the normal halide."

In a paper on the nature of the latent image, Eder[1] records a number of important facts in regard to solarization. He finds that "with pure silver bromide collodion and chemical development, solarization begins at approximately the same time as the visible blackening of the silver bromide. Solarization occurs also with physical develop-

[1] Zeit. wiss. Photographie, 3, 338 (1905).

ment; but then it usually lags somewhat behind the direct blackening.

"At 15° to 16°, nitric acid of specific gravity 1.30–1.40, destroys the solarization image on silver bromide even when only allowed to act for five minutes. The silver bromide film then gives, when developed, a rather thin but normal negative. More dilute nitric acid (sp. gr. 1.20) acts in a similar way but more slowly.

"If one takes the minimum time necessary to produce a normal, latent image on silver bromide collodion as the unit, and considers the beginning of solarization with chemical development as 300, then nitric acid (sp. gr. 1.20) destroys the normal, latent image in five minutes for exposures up to 2 or 4. After three to five minutes' action the solarization image is only partially destroyed; but it is changed very much by an attack lasting fifteen minutes, much more than the normal image, so that the film afterwards develops almost entirely as a normal image whether developed chemically or physically. Concentrated nitric acid brings about this change more rapidly and more effectively."[1]....

"These experiments also furnish the proof that the visible blackening of the silver bromide stands in no causal relation with the formation of the substance composing the solarized image. In some cases, the two phenomena seem to run parallel; but, with silver bromide containing silver nitrate, visible blackening takes place long before any solarization image is formed. With pure silver bromide collodion

[1] If a pure silver bromide collodion be moistened with water and be given a five hundred to three thousand fold exposure, the solarized image is destroyed by concentrated nitric acid (sp. gr. 1.40) acting for only five to six minutes. With chemical development there is then a normal development. The normal image due to an exposure up to 20–100 times the unit value is destroyed by concentrated nitric acid. When a longer exposure is given the normal image resists the attack by nitric acid better. With physical development the relations are approximately, though not exactly, similar. Normal images due to an exposure of 15 can be detected by this method after the nitric acid treatment. By the same test it is shown that the solarized image is destroyed, though not always completely, for here and there are to be seen traces of mixed images (half negative and half positive).

under water, the solarization image can be easily destroyed by nitric acid, while the visible, blackened product withstands the action of this acid to a great extent.[1]

"Nitric acid therefore acts in different ways on silver bromide collodion, depending on the degree of exposure which the latter has received, the difference being something as follows:

"1. The normal latent image, formed on silver bromide collodion as the result of a short exposure, is destroyed by nitric acid.

"2. The normal, negative, image due to a longer exposure is not destroyed but only weakened.

"3. The solarized, latent, positive image is somewhat attacked by dilute nitric acid and is destroyed by concentrated acid to such an extent that on development no solarized positive is formed; but, instead, a weak negative whose density depends on the length of exposure, the thickness of the sensitive film, and the nature of the development. Probably we are dealing with the super-position of two entirely different images.[2]

"With a silver bromide collodion containing silver nitrate (10 percent silver nitrate solution) solarization takes place very much less readily, a conclusion reached by Lüppo-Cramer[3] and others, and one which I have confirmed by many experiments. Solarization is noticeable only when the exposure is 3000–5000 times the unit value and even then it is much less marked than in the case of pure silver bromide collodion. It is noteworthy that the presence of silver nitrate in the film increases the total light-sensitiveness two to four-fold, while it shoves back the solarization limit to such an extent that solarization becomes marked only when the

[1] The same thing was observed by Lüppo-Cramer: Phot. Correspondenz, 1902, 694.

[2] Englisch reached the same conclusion as the result of entirely different experiments.

[3] Phot. Correspondenz, 1904, 65. (Potassium nitrite acts like silver nitrate.)

exposure is 3000–5000 times the unit exposure, thus much longer than is necessary with a pure silver bromide collodion exposed under water. The traces of silver nitrate, which cling to the silver bromide even after long washing with water, cause a very quick and dense blackening of the plate, so that the solarization is quite masked by it. A short treatment of such a plate with nitric acid (sp. gr. 1.20) after the exposure and before the development changes the plate to such an extent that solarization can readily be detected when the exposure is 1000 times the induction value. The solarization image, however, will not stand up long against nitric acid (especially a strong acid); but it is gradually destroyed so that finally a quite clear, pure negative is obtained either by physical or by chemical development."[1]

"If one exposes a silver bromide collodion plate under a scale photometer for different lengths of time from the limiting minimum way up into the region of solarization and of visible blackening, up to 3000 to 10000 times the normal exposure; and if the plate is then fixed with thiosulphate and afterwards developed physically, we find:

"1. On the portions which have received but little light, scarcely more than the induction limit, there appears a normal negative (*negative of the first order*). The substance forming the latent image withstands to a certain extent treatment with nitric acid before the development or a fixing with thiosulphate and a subsequent treatment with nitric acid.

"2. With strong over-exposure we get the *solarization image*, a positive. The limiting illumination at which this appears is undoubtedly displaced by the preliminary fixing and subsequent physical development, but the approximate point is easy to recognize, and the silver bromide is also

[1] I assume that it is well known that the solarization limit for exposed silver bromide plates can be forced back very far by the so-called retarded development (alkaline pyrogallol with a great deal of potassium bromide, for instance, develops with very little alkali, etc.). Cf. Eder's Handbuch der Photographie, 5th Ed., 3; Eder's Jahrbuch der Photographie, 17, 20 (1903).

blackened visibly at this point.[1] If applied after the fixing and before the development, moderately dilute nitric acid attacks the solarization image slowly, though more rapidly than it acts upon the negative of the first order.

"3. If the over-exposure is enormous, proceeding way beyond the first appearance of solarization, there is quite a distinct blackening of the silver bromide, which can easily be seen after the fixing and which gives rise to a negative (*negative of the second order*) when developed physically, the enormous over-exposure to the contrary notwithstanding.

"When there is a marked blackening of the silver bromide due to an enormous over-exposure, the solarized image is either above or alongside of the strongly blackened product, which last probably contains metallic silver in addition to sub-bromide. If the plate is first fixed with thiosulphate and then developed physically, the very strongly over-exposed parts develop with a blue-gray color as a negative (*negative to the second order*). At the same time the moderately over-exposed portions develop as a solarized positive, while the portions, which have received only a little light, develop as a negative (negative of the first order).

"If, however, one takes a silver bromide collodion plate which has been enormously over-exposed (3000–20000 times the induction limit), fixes it, and then treats it for several minutes with dilute nitric acid (sp. gr. 1.20), the nitric acid dissolves the substance forming the latent image of the negative of the second order (metallic silver?) and leaves behind a fairly well-defined though partially destroyed solarization image which with physical development comes out as a clear brown positive on those portions where otherwise there would have developed the blue-gray negative of the second order.

[1] The silver precipitates which form on the visibly blackened silver bromide ($AgBr + AgNO_3$) are of a bluer, more transparent color than those which form on the latent AgBr image where there is no visible blackening. Probably on the visibly blackened portions of silver bromide, the fixing sets free metallic silver which acts as nuclei for the precipitation of metallic silver during physical development over and above the nuclei due to the normal subhalide and to the solarized silver bromide image.

"The silver bromide collodion image resulting from enormous over-exposures consists therefore of three kinds of images which can be separated by fixing and subsequent treatment with nitric acid (1.20). After fixing with thiosulphate, the image due to the *visibly* blackened silver bromide, which gives a negative of the second order when developed physically, can be destroyed by nitric acid. There is then left the substance corresponding to the solarization image though somewhat attacked. On the portions which received less light the substance corresponding to the negative of the first order is left by this treatment in a state in which it can be developed.

"The behavior, therefore, of the latent, solarized and normal silver bromide images towards thiosulphate and towards physical development depends to a great extent on the degree of exposure to light, which rather inclines one to believe that probably different kinds of silver subbromide of different chemical compositions are present in the latent image or possibly that we are dealing with solid solutions having continuously varying chemical and photographic properties.

"Further, at the point where solarization is just beginning, thiosulphate changes the latent image so that it then develops as clearly solarized, even at those places where otherwise a normal negative would have been obtained, or at most only traces of solarization. When used for fixing the image before development, thiosulphate makes it possible to develop a solarized image as a normal picture or the normal latent image as a solarized picture. I was not successful, however, in determining any regularities, since the phenomena seemed to occur in a haphazard manner.

"The latent solarized image, if fixed before development, resists the action of dilute nitric acid to some extent and can still be developed. There is, however, a gradual destruction of the solarized image by the nitric acid so that the solarization limit is gradually forced back as the acid acts longer, and consequently the normal image becomes more in evidence.

Behavior of the latent image towards potassium cyanide, ammonia and ammonium bromide with preliminary fixing and subsequent physical development

"A preliminary fixing with a five percent *potassium cyanide solution* destroys most of the latent image on silver bromide collodion, so that only slight traces of it can afterwards be developed physically. A solution of potassium cyanide, to which a lot of sodium sulphite[1] has been added, is somewhat less destructive; but the slight residue of the substance forming the image which survives is easily destroyed by nitric acid and then physical development yields no result. Probably cyanide of potash is more effective than thiosulphate in splitting the sub-bromide into the soluble silver bromide and metal, so that nitric acid dissolves what is left of the image.

"*Ammonia as a fixing agent* acts like thiosulphate. It is easy to see that ammonia dissolves the illuminated silver bromide more slowly than it does that which has been exposed to light. I have myself confirmed this fact first recorded by Englisch.[2] The color of the silver bromide, which has been exposed to light for only a short time and which contains the substance forming the latent image, is identical with that of silver bromide which has not been exposed, and consequently the latent image cannot be detected by the eye. What remains of the image after the preliminary fixing with ammonia can be developed physically very well so that ammonia is not as effective as thiosulphate in decomposing the silver subbromide or, to put it in a better way, the substance forming the latent image. Instead it probably leaves a large part of the hypothetical subbromide intact and consequently this residual latent image withstands the action of concentrated nitric acid fairly well.

[1] Recommended by Lüppo-Cramer because the mixture of sulphite and cyanide attacks metallic silver much less readily in presence of air than does a pure solution of potassium cyanide. Eder's Jahrbuch der Photographie, 17, 43 (1903).

[2] Zeit. wiss. Photographie, 2, 516 (1904); Eder's Jahrbuch der Photographie, 19, 363 (1905).

"If we start with washed silver bromide collodion and expose the silver bromide to a strong light until it is blackened visibly, we shall find that ammonia, like thiosulphate, precipitates so much metallic silver during the fixing process, that this silver interferes with the phenomenon of development—physical development—and that only after this metallic silver has been removed by nitric acid (sp. gr. 1.20) does one see clearly the solarization effects always present in a silver bromide collodion plate which has been over-exposed so enormously.

"A saturated *solution of ammonium bromide* can also be used as a fixing bath for silver bromide. Silver bromide collodion plates come out clear from this bath and after this preliminary fixing there remains a slight residual image which can be brought out by physical development. This was first noticed by Lüppo-Cramer[1] and my experiments confirm his statement except that I found that the destruction of the latent image by ammonium bromide was more nearly complete than when thiosulphate was used. The portions of the silver bromide receiving but little light were especially strongly attacked, which is not surprising since Lüppo-Cramer[2] found that solutions of bromides in general weaken considerably and partially destroy the latent image on silver bromide collodion (reverse formation of normal silver bromide from subbromide). For this reason the latent image after the preliminary fixing may be only a very small fraction of the original latent image. If the silver bromide collodion plates are very much over-exposed, to the point of marked solarization, traces of the solarization image can be brought out by physical development after the plate has been fixed."

"Even when there is a preliminary fixing with ammonium bromide and a subsequent physical development, it is possible, by taking pains, to establish the existence of a negative of the first order, of a solarization image, and of a negative

[1] Phot. Correspondenz, 1901, 418.
[2] Ibid., 1902, 635.

of the second order. These residual traces of images react with nitric acid in much the same way as do the latent images which have had a preliminary fixing with thiosulphate.

"In consequence of this proof that the residual traces of the latent silver bromide image, which result from a preliminary fixing, do not vary in any definite way with the sulphur content of the fixing medium, we are justified in rejecting, as the most insufficient of all such theories, the one put forward by Precht,[1] without any decent foundation, to the effect that silver sulphide (*silver sulphide theory*) is the substance forming the latent image after a preliminary fixing.

Proof by spectrum analysis that the substance forming the latent image is independent of the wave-length of the light

"If one lets the solar spectrum (quartz spectrograph) act on a silver bromide collodion which has been made sensitive for greenish-yellow, red or green by means of eosine, ethyl violet or some similar color sensitizer, it is well known that one can develop the normal image equally well chemically (for instance with an alkaline hydroquinone solution) or physically (iron vitriol and silver nitrate).

"If one treats the latent image of the spectrum with a sodium thiosulphate solution and if one then develops the film physically, it is possible to develop such a latent image, after fixing, over the whole spectrum for which the sensitized plate would have been sensitive under normal development.

"When the plate has been very much over-exposed, the preliminary fixing leaves just as easily developable traces of the latent image in the portions where the maximum of sensitiveness occurs, in the yellow-green or the red, as it does in the violet or the ultra-violet. When treated with nitric acid in a way similar to that of the previous experiments, the substance of the latent image showed no effect

[1] Cf. Eder: Phot. Correspondenz, 1900, 667; Lüppo-Cramer: Ibid., 1901, 358, 418; Schaum: Phys. Zeit., 1901, 536, 542; Eder: Chemiker Zeitung, 1904, 1005.

due to the wave-length of the reacting light in so far as any qualitative behavior towards chemical agents was concerned.

"From this it follows with great probability that silver bromide plates treated with eosine or other sensitizing dye undergo the same photochemical reaction in the region of the induced light-sensitiveness (yellow-green for instance) as in blue, violet or white light, at any rate as far as the formation of the *normal latent image* is concerned. It is doubtful whether this is also true for the *solarization phenomena*[1] in the red end of the spectrum; but I have not yet been able to settle this question conclusively.

The latent image on silver iodide

"*Silver iodide*[2] in the form of the 'wet collodion plate,' as used in making reproductions, acts very like silver bromide. If silver iodide collodion is first dipped in a silver nitrate solution and then exposed to light, a ferrous sulphate solution will bring out a latent image after an exposure to daylight equivalent to an optical intensity of about 6–10 second-meter-candles (induction limit). With the Welsbach light which contains less violet, an exposure of about 200 S. M. K.[3] is necessary to reach the induction limit. The latent image on silver iodide is but little attacked by nitric acid (sp. gr. 1.40) in six to ten minutes, and still less by more dilute nitric acid (sp. gr. 1.20). After this treatment with acid, the latent image can still be readily developed physically by means of ferrous sulphate and silver nitrate solutions.

[1] When silver bromide collodion is sensitized for green by means of eosine silver, it is easy to obtain normal negatives of the spectrum. After standing for a few days, however, such an emulsion undergoes a spontaneous decomposition in the dark to such an extent that the silver bromide, even without exposure to light, is reduced by the developer and fogs just as though the film had been exposed. When these silver bromide emulsions, which have changed in the dark, are exposed to sunlight and then developed, they show distinct solarization phenomena, like previously exposed silver bromide plates and these phenomena are more marked in the blue and violet than in the green. These same solarization images occur even when the plates are first fixed with thiosulphate and then developed physically.

[2] Eder: Rezepte und Tabellen., 6th Ed., 1906, 26.

[3] [Second-meter-candles.]

"If the latent silver iodide image is first fixed with thiosulphate solution and then developed physically, it turns out to be partially destroyed, up to about 3–5 times the minimum exposure.[1] If the latent image on the silver iodide is first fixed with thiosulphate, then washed and afterwards treated with nitric acid for five or six minutes, the image is destroyed up to exposures of about 25–40 times the minimum. Portions, which have received more light, come out perceptibly with physical development, though the resulting image is considerably weakened.". . . .

"The substance of the latent *solarized* image with silver iodide plus silver nitrate solution (wet collodion process), attracts less silver during physical development than does the image resulting from normal illumination; there is thus definite solarization. Aqueous chromic acid destroys both the solarized and the normal latent image to about the same extent[2] (different from silver bromide). Both forms (the normal as well as the solarized latent image) resist a thiosulphate solution at least to the extent that they afterwards respond to physical development. In spite of this the thiosulphate has actually caused an important chemical change in the nature of the latent image. Originally the normal latent image, resulting from a sufficient exposure, withstood the action of nitric acid very well. After the preliminary fixing with thiosulphate solution, the image is completely destroyed by nitric acid (sp. gr. 1.20) acting for only five minutes. On the other hand, the latent *solarization* image on silver iodide, after fixing with thiosulphate, resists nitric acid for a short time to such an extent that a solarized image may afterwards be developed physically. If the nitric acid acts for a longer time, however, there is such a change that a normal negative develops instead of the solarization image. These reactions make it probable that the latent, developable image on silver iodide collodion consists of silver subiodide

[1] The figures vary a good deal with the time that the thiosulphate acts and the nature of the developer subsequently used.

[2] Ede Photr.. Correspondenz, 1902, 645.

which is decomposed by thiosulphate almost completely into silver iodide and metallic silver (different from the behavior of the hypothetical silver subbromide in the latent image).

Explanation of the recorded phenomena in terms of the subhalide theory

"The subhalide theory is able to explain without difficulty the complicated experimental behavior, toward chemical reagents, of the latent image in a silver bromide film:

"*The substance of the normal latent image* (*negative of the first order*) consists of silver bromide reduced in varying amounts to subbromide.

"We assume further for the case of progressive illumination that, in consequence of a photochemical setting free of bromine, at the beginning of the exposure to light there is found a silver bromide corresponding very closely in composition to normal silver bromide. This subbromide, however, as we see from the process for making photographic negatives is more rapidly reduced by reducing agents to metallic silver than is the pure unexposed silver bromide. This modification of subbromide is destroyed by thiosulphate as well as by nitric acid. By means of this assumption we explain all the phenomena recorded in regard to the latent silver bromide images which result from very short exposures.

"With a somewhat longer exposure there is formed a silver subbromide which constitutes the latent image of the normal negative. It is only slightly attacked by nitric acid. With increasing exposure it yields on development a normal negative with the normal characteristic blackening curves corresponding to it. This silver bromide is less readily soluble than silver bromide in solutions of the fixing media, such as ammonia, ammonium bromide or thiosulphate. After the preliminary fixing of the latent image this subbromide therefore remains as a residual image which can be developed physically in spite of its having undergone certain changes. Depending on the chemical nature, the

concentration, or the temperature of the fixing bath, this silver subbromide is developed more or less completely into the soluble silver bromide and undissolved metallic silver so that the residual image consists of subbromide mixed with more or less of metallic silver. Potassium cyanide causes the greatest decomposition and with it the residue consists of metallic silver only.

"If one allows nitric acid to act on the latent image after it has been fixed, the substance forming the image is destroyed still more, the destruction being greater the more completely the image consists of metallic silver. Since the silver is dissolved, more or less of the image will be removed and there will remain behind some subbromide, the presence of which can be shown by physical development. But even this is broken down, by a continuous treatment with concentrated nitric acid, into silver which dissolves and silver bromide which does not respond in the dark to physical development, but which at once forms new nuclei for physical development if it is exposed to light and this converted again into a developable subbromide.

"With a very strong over-exposure of the silver bromide there is formed a *solarization image*, the substance of which is not identical with the directly blackened silver bromide which is apt to be formed at the same time. This substance has a different chemical composition and different chemical properties from the substance forming the negative image of the first order.

"With more intense over-exposure and subsequent development we get the negative of the second order. The latent image from which this was formed probably consisted of a mixture of at least three chemically different substances, namely of metallic silver, of the substance constituting the solarization image, and of the subbromide constituting the image which yields the negative of the first order. All these substances are shown to be present not only by their photographic behavior towards the photographic developer, but by their different chemical behavior towards thiosulphate,

ammonia, nitric acid, etc. The substance formed by the direct blackening of silver bromide in light shows a different photographic action from that of the latent or the solarized image. This can be explained less well on the assumption of a solid solution of variable amounts of Ag_2Br in silver bromide. It is more probable that different modifications of silver subbromide occur in the differently illuminated portions of the silver bromide film.

"The latent image on silver iodide with an excess of silver nitrate seems also to consist of silver subbromide, which, however, seems to be more easily decomposed into metallic silver and silver halide than is the case with silver subbromide.

"The substance forming the normal latent image on silver bromide does not vary in its qualitative behavior towards chemical reagents with the wave-lengths of the light that produced it. Color sensitizers (eosine, ethyl violet, etc.), which make silver bromide light-sensitive to light of longer wave-length, force the silver bromide to the same photochemical reaction of the silver subbromide formation in the production of the latent image which is characteristic of silver bromide by itself in the blue, violet and ultraviolet regions of the spectrum."

Abney believed that the forcing-back of the solarization, when potassium nitrite is added to the film before exposure, is due to the reducing action of the potassium nitrite. Lüppo-Cramer[1] maintains, however, that the only action which nitrites, sulphites and silver nitrate have in common is that of accelerating the splitting off of bromine from the silver bromide. Being "chemical" sensitizers they increase the light-sensitiveness of the plate, but Lüppo-Cramer feels that we do not know at all why they prevent solarization.

"Wilbert[2] made experiments with silver bromide plates which were exposed beyond the solarization limit. With an exposure of one minute to diffused daylight under a dense

[1] Phot. Correspondenz, 1904, 65.

[2] Eder's Jahrbuch der Photographie, 17, 461 (1903).

diapositive, there was partial solarization; with exposures of from four to eight minutes there was complete solarization with but slight differences due to the length of exposure. In the camera an exposure of one-half second gave a normal negative; with a larger stop and a longer exposure, eighty times the amount of light still gave a negative, though a flat one, when the plate was developed with the same metol-hydroquinone developer. With eight times as much light the plate was in the so-called zero state, being pretty thoroughly fogged, but showing signs of reversal. With ten thousand times the amount of light, a completely reversed, solarized image was obtained, the development taking place in the dark and lasting three minutes. A similarly over-exposed plate was developed in diffused daylight and a solarized image was also obtained, but the development took three times as long.

"Among the developers, the least suitable for bringing out solarized pictures were: pyrogallol, amidol, eikonogen, metol. These work too rapidly and consequently irregularly. Hydroquinone is much better, either with or without alkali; in the latter case the picture is reddish-brown.

"The reversal of under-exposed negatives has been studied by A. Guébhard,[1] who found that positives can be obtained from moderately sensitive, under-exposed plates provided these plates are developed slowly. As developer, he used a solution of the following composition: 3 g anhydrous sodium sulphite, 1 g pyrogallol, 3 g sodium carbonate in one liter of water. Guébhard worked at a temperature of 8° C and drew the following conclusions from his experiments:

"1. When under-exposed plates are developed slowly, the reversal begins at those points which received the least light.

"2. With two under-exposed plates, one of which had been exposed twice as long as the other, the reversal occurred much quicker on the plate which had had the shorter exposure.

[1] Eder's Jahrbuch der Photographie, 19, 388 (1905).

"3. In a normal developer a plate, which gave a good negative in two hours, was only half reversed in six hours and then with a formation of a thick fog.

"4. Provided an over-exposure does not reach the point of the ordinary reversal, it does not help this new reversal but rather retards it very much."

In 1890 Waterhouse found that the addition of small amounts of phenyl-sulpho-urea to the developing bath caused a reversal. In a paper[1] read before the Asiatic Society of Bengal in April, 1891, Waterhouse said:

"At the meeting of the Society in August last, I exhibited some specimens of a curious reversal of the photographic image produced by adding small quantities of thio-carbamides or sulpho-ureas to the ordinary eikonogen developer, and showed that although reversal of the image was by no means uncommon, it was usually caused by over-exposure or some other abnormal action of light, whereas to produce these new reversals even less than the ordinary exposure was sufficient, and they appeared to be entirely due to some peculiar action of the thiocarbamide added in very minute quantities to an alkaline eikonogen developer.

"At that time I was quite unable to offer any opinion as to the probable cause of these reversals, or as to how they were produced, beyond stating the probability that, although there were many points of difference, they would be found to be in accordance with the generally accepted theory worked out by Capt. Abney, and were due more or less to oxidation or rehalogenization of the exposed parts of the film, and that owing to the peculiar reducing action of the alkaline thiocarbamides the film during development was practically in the same state as if it were over-exposed. It seemed also probable that sulphur was the active agent in producing reversals.

"Further work with these curious salts and especially

[1] Major-General Waterhouse was good enough to send me reprints of several papers of his, on solarization, this one among others. These reprints have been of great assistance to me in preparing this paper.

with a compound salt of thiocarbamide and ammonium bromide, discovered by Prof. J. E. Reynolds in 1868 and called by him tetrathiocarbamid-ammonium bromide, which was found to be exceedingly active in producing perfect reversals of the image with very short exposures, led me to the belief that this complete change of deposit from the lights to the shadows of the photographic image must be more or less due to electro-chemical action. The subject of electrochemistry is one of which I have little knowledge, but I have been able to make some simple experiments from which, though not conclusive, it seems probable that my surmise is correct, and so far as they go, they seem to establish that not only, as former observations by Lermontoff, Eder and Abney had shown to be probable, is the ordinary process of photographic development of sensitive surfaces containing silver haloids, accompanied by electrical action, but that the addition of these minute quantities of thio-carbamides to the developer, greatly increases the intensity of the electrical action and produces a reversal of the current which should also account for the reversal of deposit.

"With the aid of a very sensitive galvanometer, which has been kindly loaned me by the Rev. Fr. Lafont, S.J., who also assisted me in the experiment, it was found that when a pair of pure silver plates coated with finely precipitated silver bromide, one of which had been exposed to light and the other not, were connected to the galvanometer so as to form a galvanic couple and immersed in the ordinary eikonogen developer, the exposed plate formed the negative pole and the needle was deflected to the left, while in the developer containing a little thio-sinamine, the exposed plate formed the positive pole and the needle was deflected to the right.

"This experiment has been successfully repeated several times with several plates prepared in the same way and with other thio-carbamides, also with silver plates bromized by dipping them in bromine water; and so far the occurrence of the reversal is well established.

"I have also tried the same experiment with ordinary dry plates rendered conductive in various ways, the best of which appears to be gold leaf applied either on the face of the film or behind it. Gelatine offers very great resistance to the current, and though I have obtained distinct evidence of currents in both directions, they are not always observable, nor is it quite certain that they are caused by electrolytic action within the gelatine film, and further investigation as to this is necessary.

"I have also found that reversals of the reduction products, somewhat similar to those obtained by photographic methods, may be obtained entirely without the agency of light by passing a current from a single bichromate cell through a pair of silver plates coated with silver bromide and immersed in eikonogen developers prepared with or without thio-carbamides. In this case the plate attached to the carbon pole in the plain developer showed only a very little black deposit, while the plate attached to the zinc pole showed a very strong dark deposit all over. A pair of similar plates immersed in some of the same developer to which a few drops of a solution of thio-sinamine had been added showed quite different results, the plate attached to the carbon pole showing a strong black deposit, while the plate attached to the zinc pole was almost clear on the face and free from deposit, showing only a slight tarnish, caused by sulphur. I have some plates of this kind here, though the reversed effect is not quite so strong as it was on my first plates. I have found it difficult to obtain such marked reversals again though I quite believe they are obtainable and the best conditions for securing successful results have yet to be ascertained.

"Some similar effects were produced on Eastman's bromide paper and on ordinary dry plate films to the silver plates.

"Although results obtained with silver bromide on silver plates are not quite comparable with those obtained with ordinary gelatine plates, these experiments show that

under favorable circumstances the action of developing solutions on silver bromide is accompanied by distinct electric action, and that these thio-carbamide reversals may be produced by electrical methods and are attended by a reversal of current. How this reversal of current is brought about is not yet quite clear, but seems to be explained by some observations on metallic sulphides, by W. Skey, recorded in Vol. XXIII of the *Chemical News*. He found that sulphides which have the power of conducting can also generate electricity and that silver sulphide is positive to metallic silver. In a battery consisting of a sulphide and a metal in acidulated water, the gas liberated is sulphuretted hydrogen, the nascent hydrogen exerting a desulphurizing action upon the metallic sulphide, the ultimate effect of which is in some cases to completely reduce the mineral to the metallic state. He also shows that these sulphides are capable of performing the functions of the negative element of a galvanic couple.

"It seems probable, therefore, if electrolytic action does take place in gelatine films during the process of photographic development, that, according to the laws of electrolysis, with the ordinary developers the exposed parts of the plate form the negative pole and attract the metallic elements and hydrogen, while the bromine, or other halogen and acid radicals, with the hydroxyl go to the unexposed parts forming the positive pole.

"On the other hand, with the alkaline thio-carbamide developers, at the same time that silver is reduced on the exposed parts, silver sulphide is formed on the unexposed parts which then become the negative pole and attract the sulphur, the hydrogen and some of the silver from the exposed parts, while the halogen and hydroxyl pass to the positive pole and transform part of the remaining silver into silver haloid which is dissolved in the fixing bath.

"Although this theory, as stated in a rough way, seems to agree fairly well with the facts, and from the experiments I have made seems probably the correct explanation of the

reversals, I do not feel myself yet able to put it forward authoritatively, and a great deal of further investigation is required. The subject is a very difficult one beset with uncertainties, and requires more time and close attention than I have been able to give for working it out fully."

It is clear by this time that the effect due to an over-exposure may be modified profoundly by the treatment which the plate receives after exposure. In the following paper Precht[1] goes one step further and claims that solarization is a phenomenon of development only.

"From the law of mass action it follows necessarily that the splitting off of bromine from silver bromide under the influence of light must eventually lead to a state of equilibrium, and then the reaction will proceed no further. This is not changed at all, even if one assumes that a second reaction takes place between the bromine set free and the binding material of the film. The blackening curve of silver bromide gelatine must therefore end with the maximum possible density, with the so-called neutral zone. This is not the case, however, and one observes the phenomenon of reversal of solarization. Some work by Englisch on the lesser effect of intermittent illumination has rather led to the view that in the light there are two distinct kinds of change, one a normal and the other a solarizing change. Now films which have been much over-exposed and which are developed normally, show solarized and normal particles side by side. If such films are developed very slowly, they show normal pictures and no solarization. It has, however, been impossible so far to show a solarizing change due to light which has occurred quite independently of the normal change. On the other hand, Abney's experiments have proved conclusively that solarization can be checked by the presence during the exposure of certain reducing agents, such as potassium nitrite, and can be increased by the presence of oxidizing agents. It seems therefore quite possible to simplify

[1] Internat. Kongress angew. Chemie, Berlin, 4, 351 (1903).

our conceptions and to consider that solarization takes place entirely in the time *after the exposure.* When the action of the light has ceased, the bromine set free can convert the photobromide back into normal bromide which is more difficultly reducible and therefore causes the phenomenon of solarization. Of course such a conception has no other value than that of a working hypothesis.

"This conception has the special advantage of making the lesser effect of intermittent illumination intelligible. To test it more fully I have extended to silver bromide gelatine the experiments of Abney which referred especially to collodion emulsions. These experiments are closely allied to the earlier experiments on the use of acetone bisulphite in a retarded developer. Apart from the fact that the acetone bisulphite, like any acid sulphite, decreases the reduction velocity by neutralizing partially the alkali of the developer, there are other reactions which are probably the important ones. I have previously called attention to the fact that acetone bisulphite reacts with the oxidation products of the developer and therefore acts as a reducing agent. This is confirmed by a number of experiments in which plates were bathed in a 1–5 percent solution of acetone bisulphite, dried, and then exposed to intense light. When these plates are developed in a normal developing solution, it is seen that the amount of solarization is surprisingly small. Even the sun's image is only reversed with difficulty. At the same time another change becomes evident, the formation by tanning of large grains when the amount of acetone bisulphite is high. This tanning action is also one to which I have previously called attention. It decreases the diffusion in the film and I look upon this as the essential reason for the advantages due to this compound in the case of a retarded developer, though of course all three causes work together.

"A long time ago Abney[1] called attention to the fact that strongly illuminated portions of ordinary silver bromide

[1]Treatise on Photography, 1893, 309.

swell less readily than the other portions. This is always very noticeable if one lays in water a plate which has received a long exposure to the sun.

"It appears to be important to establish that no solarization can occur if the developer is already present in the film at the time of exposure. To carry out the experiments the plates were saturated with a developer solution containing no alkali, and afterwards dried. They were then exposed to any bright source of light for a suitable time (long enough so that with ordinary plates and ordinary developer, solarization would be very marked, and were developed simply by being laid in a soda solution.[1] No solarization can take place so long as there is any unchanged reducing agent on the high lights. The following experiment, for instance, shows how far this holds: On an ordinary plate, lay one impregnated with developer, and on the film of the latter lay a piece of metal with holes cut in it. Expose to full sunlight for five minutes and then develop. The impregnated plate shows an ordinary negative while the normal plate is completely solarized even though the light falling on it has passed through the impregnated plate.[2] This result is entirely in accord with Abney's experiments and with the theoretical ideas I have outlined. There are, however, a number of necessary consequences which must still be tested."

Eder[3] comments as follows on this theory of Precht's:

"It is well known that the blackening in the developer of a silver bromide gelatine plate, which has been exposed to the light, increases only up to a certain maximum exposure and decreases if exposed for a still longer time. This phenomenon is called "solarization." It is also well known that the appearance of solarization can be checked by a suitable development, by using weak developers or developers

[1] I have been informed that the technical use of such a process has been patented by the Farbenfabriken vorm. Friedr. Bayer and Co., Elberfeld.

[2] This experiment was first tried by Herr Süss.

[3] Eder's Jahrbuch der Photographie, 17, 20 (1903).

whose rate of reduction has been decreased by addition of restrainers (such as potassium bromide) or by a suitable change in the proportions of the developer. Under this we must also include the developers with a decreased alkali concentration such as the pyrogallol-sulphite developer without alkali or the edinol developer with acetone sulphite and very little alkali, as recommended by Precht. When the over-exposed plate is developed there first appears a normal negative which on further development changes into a solarized image (positive). *This is the usual phenomenon on developing* partially solarized plates.

"The theory of this phenomenon has hitherto been considered to be that in the solarized plate some other photochemical change in the silver bromide gelatine has taken place than that occurring in a normally exposed negative, that the two types of light images are superposed, and that one developer brings out the one image the more rapidly and another developer the other image, so that it is possible by a suitable choice of the developer to keep the solarization phenomenon (change of negative into positive) within any desired limits or to check it entirely.

"Precht[1] makes the assertion: Solarization is exclusively a phenomenon of development which has no necessary connection with the photochemical change of the silver bromide.

"This theory is however false and entirely unfounded, as I have shown,[2] for its experimental foundation is bad and it can only have arisen through ignorance of the literature of the subject.

"It is well known that a normal development can be obtained by a chemical treatment of silver bromide which has been over-exposed to the point of solarization. It is only necessary to treat the over-exposed silver bromide film with certain chemical reagents before developing and then to develop with an ordinary developer. Thus one can get a nor-

[1] Phys. Zeit., 1902, 426.
[2] Phot. Correspondenz, 1902, 570.

mal negative with the same developer which (without the previous treatment) gives a solarized picture.

"I will run over some characteristic experiments on the phenomenon of solarization which were recently described.[1] It is easy to prepare solarized plates if one places a dry plate in a Chapman-Jones scale photometer[2] and exposes it for ten to sixty minutes to a gas light at a distance of 40 to 50 cm.

"The silver bromide gelatine plates[3] used by me behaved as follows with an ever-increasing exposure:

H. M. S.	Necessary quantity of light in candle-meter-seconds.
First appearance of latent normal image (induction limit)	0.1
Powerful half-tone of normal negative	1.3
Deep blackening in the lights	8–10
Beginning of the direct photographic blackening[4]	3000–10000
Beginning of solarization at limit of neutral zone[5]	27000–40000
Satisfactory reversal	300.000 and over.

"If one takes as unity[6] the amount of light necessary to produce a normal negative, my experiments show that, with a pyrogallol-soda developer and no potassium bromide, there is a marked appearance of solarization for an exposure of 3000, while a fairly thorough solarization calls for an exposure of 10,000 or even 30,000. These figures vary a good deal with the nature of the plate.

Forcing back of the solarization limit by retarded development

"If one uses a very slow-acting developer, to which restrainers, especially potassium bromide, may be added if

[1] Phot. Correspondenz, 1902, 645.

[2] Ibid., 1902, 430.

[3] Commercial plates of medium sensitiveness.

[4] Varies very much with the nature of the plate.

[5] Varies with the time of development and the use of the ordinary metol developer or of pyrogallol.

[6] About 10 candle-meter-seconds (H. M. S.) with my dry plates.

necessary, the limit of solarization can be forced back very much and the greatly over-exposed portions of the silver bromide plate may be developed as a normal negative even though they would solarize with the ordinary developers.

"If one develops such a plate with a pyrogallol-soda developer to which 1–10 percent of crystallized potassium bromide has been added, the solarization limit is forced back considerably. It is forced back still more by the mixture of edinol developer (1 : 25) with one percent solid acetone sulphite[1] as recommended by Precht, but the pyrogallol and potassium bromide gives a stronger negative with better gradations in the region of great over-exposures, well beyond the solarization limit. The same is true of many other developers.

"With respect to the rate of development of over-exposed plates, I mention merely that it is well known that many developers without alkali develop the latent image very slowly and that they act more energetically with increasing amounts of alkali.

"One should not be misled, however, into considering solarization exclusively as a development phenomenon.[2]

Forcing back the solarization limit on over-exposed dry plates by treatment with chromic acid before development

"Aqueous solutions of bromine change the solarized image into a silver bromide gelatine which develops as a normal negative. If the bromine acts for a longer time, both images are destroyed. Lüppo-Cramer[3] made this observation for collodion emulsion and for gelatine plates, with which last, however, there is a disturbing tanning of the gelatine. Then Schaum and Braun[4] found that ammonium persulphate not only destroys the latent image but also removes the solarization. Solarized silver bromide gelatine films develop

[1] Phot. Correspondenz, **1902**, 570.

[2] Cf. Phot. Correspondenz, **1902**, 569.

[3] Wissenschaftliche Arbeiten auf dem Gebiete der Photographie, 106 (1902). Cf. also Phot. Correspondenz, **1901**, 134.

[4] Phot. Mittheilungen, **1902**, 224.

normally with hydroquinone if they have been soaked for twenty-four hours in a 2–5 percent persulphate solution. I found that in aqueous solution chromic acid[1] (1 g potassium bichromate, 3 g sulphuric acid and 100 cc water) works in a similar way but more rapidly and in a very reliable manner. This solution destroys the weak normal latent image[2] and decreases the solarization enormously. The highly solarized silver bromide is changed after fifteen minutes' action into a state which permits the development of a normal negative,[3] instead of a solarization diapositive.

"During this change the visible photographic blackening on the over-exposed plate is partially destroyed for the weaker ranges of the sensitometer. The remaining blackened portions can be developed after the treatment with chromic acid, but as a normal negative and not as a solarized image.

"With a mixture of concentrated chromate solution and nitric acid (for instance, 2 g potassium bichromate, 6 cc concentrated nitric acid and 100 cc water), exceptionally strong solarization effects may be overcome by letting the solution act for one-quarter to three-quarters of an hour. When such an over-exposed plate is washed and developed for instance with the ordinary metol-soda developer, fifteen to twenty minutes' developing will bring out a negative free from fog and with good gradations, running from No. 1 to 13 or even 20 numbers of the Jones sensitometer, depending on the length of time the acid is allowed to act. Without the chromate treatment, the same developer would have developed a similarly over-exposed plate so as to produce the strongest solarization phenomena and a good deal of fog.

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[1] First used by me in 1881 to remove fog. Phot.-Archiv (1881).

[2] This is true, for instance, for dry plates which on development give a blackening from 1–16 of the Scheiner sensitometer. Such latent images are completely destroyed by chromic acid.

[3] For the destruction of the solarization image by partial fixing with sodium thiosulphate, see Englisch: Eder's Jahrbuch der Photographie, **16**, 73 (1900).

"In Figs. 5 and 6[1] are the facsimiles of silver bromide plates exposed up to strong solarization and developed, one before and the other after a treatment with chromic acid. Fig. 5 shows the solarization image resulting from the ordinary development. Fig. 6 shows the partial forcing back of the solarization limit due to treating for fifteen minutes with bichromate and sulphuric acid, and then developing. In places there is a normal negative, and the general fog, due to irradiation and to halos, is partially destroyed. In Fig. 7[1] we have the complete reversal of the solarization image, after the treatment with bichromate and nitric acid, into some thing which develops as a normal negative. All the plates were developed with the same metol developer.

"This treatment of solarized plates with chromic acid is more effective as a means of removing solarization effects than the mere variation (retarding) of the developer. This proves anew what Lüppo-Cramer had already shown that it would be false to consider solarization exclusively as a development phenomenon. As a matter of fact, by treatment with chromic acid, solarization can be eliminated over very wide ranges without changing the composition of the ordinary developer in the slightest. Furthermore, all the other methods which I have recommended for eliminating solarization, work well and in a reliable manner."

In the lecture before the Camera Club to which reference was made in the beginning of this paper, Waterhouse calls attention to the fact "that Dr. Luther has quite recently enunciated the theory that solarization is caused by free bromine hardening the gelatine, and so rendering it impermeable to the developer in the most exposed parts; so that, in some cases, the silver bromide is reduced more quickly on the less exposed parts than on the most exposed, and the result is the production of a transparent positive. By retarding development in various ways, this tendency to reversal may be overcome. This theory, though possibly ap-

[1] [Not reproduced in this paper.]

plicable to gelatino-silver bromide dry plates could not be so to the cases of reversal with other forms of sensitive plates in which the same phenomenon is observed.

"Dr. R. Englisch has pointed this out.[1] He says that if we have to do with the hardening of the gelatine film, the diffusion of solutions will be affected. Assuming that by prolonged exposure the subbromide is actually formed, the amount of bromine set free will increase with the length of exposure, and will exercise a strong hardening effect on the gelatine. The fixing solution will therefore be able to dissolve less silver bromide from the hardened parts than from the unaltered parts, and if a plate treated in this way is then developed a reversal of the image must result. By adding sodium thiosulphate to the ferrous oxalate developer, Eder obtained reversed images upon over-exposed plates. What happens in that case is not quite known, but here it depends directly on the reversed and separate actions of the fixing medium and developer. Englisch then describes an experiment in which rapid dry plates were exposed to magnesium light in slips with normal and over-exposures sufficient to produce solarization and loss of density. After exposure the plates were divided in two. One set was developed, and the other placed in a 10 percent solution of hypo for measured periods from 1 to 5 minutes, and then developed with metol soda, until the maximum density was attained. With the plates that had been in the hypo for 5 minutes, the slips which showed the greatest density on the directly developed plates showed clear glass, while the slips which were solarized on the developed plates developed with full density on the partially fixed plates. The full density of these plates was quite destroyed, but the sequence of the densities was entirely reversed, so that the solarized parts were the densest, and the normally exposed were the thinnest."

In a paper before the Berlin Congress of Applied Chemistry, Englisch says:[2]

[1] Archiv. wissenschaftliche Photographie, 230.

[2] Internat. Kongress angew. Chemie, Berlin, 4, 423 (1903).

"The normal development of slightly solarized films by means of acid sulphites is looked upon as the result of the prevention of the diffusion of the developer where the gelatine has been made insoluble at the solarized portions. The blackening is due to the slow diffusion of the developer, to its decreased reducing power owing to the acidity, and to its retarded action. It is believed that in the retarded normal development only the normally changed silver bromide grains at the surface are reduced. In contrast to this the normally changed portions are first oxidized when bichromate is applied, and the solarized portions are all that remain available for the subsequent development. The same thing occurs in the partial fixation, previously suggested by the author, in which the normally changed portions are dissolved before the solarized portions.

"Just where solarization begins, intermittent illumination gave clearer, apparently more completely changed portions than a continuous illumination of the same period. That was explained on the assumption that the simultaneously occurring normal and solarizing changes must both take place to a lesser extent with intermittent illumination; but that the normal changes will vary markedly and the solarizing changes but little from those under continuous illumination. Since the lesser difference in the solarization causes a greater blackening and that of the normal change a greater blackening, the difference between the two will be what counts. If only the normally affected portions are developed by means of a retarded developer, the difference in blackness between the two effects of light will be greater, while they will be smaller if only the solarized portions are alone developed by means of oxidation.[1] This expectation was confirmed by experiments. It appears also that the lighter and darker stripes which appear with a retarded development are surface stripes, but that the variations in blackness which ap-

[1] [I don't know what this passage means and this may have affected my translation of it. The reader is therefore advised to refer back to the original.—W. D. B.]

pear during the normal development of a solarized plate are determined by the relations between the surface and a certain thickness of the film; they represent the integral of the prevailing conditions varying periodically with the illumination."

In an admirable paper from Luther's laboratory, Weisz[1] shows that a hardening of the gelatine is not the cause of solarization and that the explanation of the phenomenon must be sought elsewhere, "presumably in an actual chemical change in the nucleus of the latent image." Weisz goes on to say that the results of his experiment, No. 16, show that the strong oxidizing agents convert the substance forming the solarized image into something which can form solid solutions with silver. He points out that, according to Schaum, treatment with persulphate causes a normal development of solarized films. He then adds that "the fact that solarized layers give normal pictures when developed physically after being fixed (experiment No. 17*b*) shows that the substance forming the latent solarized image decomposes in presence of sodium thiosulphate into silver and something which is soluble in thiosulphate."

That there is still a radical difference of opinion as to what causes solarization is shown by a recent paper by Homolka[2] in which an entirely different explanation is given.

"In several papers which have appeared in *Phot. Correspondenz* during the current year, I have shown that one can develop the latent image on silver bromide gelatine by means of indoxyl or thioindoxyl and that the negative picture thus obtained is not homogeneous, but consists of a silver image and an indigo image. The two images can be separated without difficulty. If the developed and fixed plate is treated with a potassium cyanide solution, the silver image dissolves while the blue indigo image (or the red thio-indigo one) remains. However, if one treats the developed and fixed plate with an alcoholic sodium hydrosulphite solution, the

[1] Zeit. phys. Chem., **54**, 344–350 (1906).

[2] Eder's Jahrbuch der Photographie, **21**, 58 (1907).

indigo picture dissolves as 'indigo-white' while the black silver image remains. From these facts we draw the conclusion that the substance of the latent image also is not homogeneous but must contain two constituents. One of these I consider a silver perbromide, perhaps $AgBr_2$; it can oxidize indoxyl to indigo and thus causes the 'indigo image.' The other constituent is very probably a silver subbromide or the corresponding mixture of Ag + AgBr; under the action of indoxyl it is reduced to metallic silver, which presumably acts as a silver nucleus and causes the formation of the 'silver image.' In the following way it proved possible to prepare the two constituents of the latent image separately by purely chemical methods without the intervention of light. If an unexposed dry plate is treated with very dilute bromine water, there is formed a latent perbromide image which develops in an indoxyl bath to a pure blue 'indigo image.' On the other hand, if one treats an unexposed plate with a very dilute stannous chloride solution, there is formed a 'latent subbromide image' which develops in the indoxyl bath to a black 'silver image.' As a result of these experiments I adopted the view that the latent image is formed according to the following equation:

$$3AgBr = AgBr_2 + Ag_2Br.$$

The film of a silver bromide gelatine dry plate, after exposure to light, consists therefore of the following three substances:

"1. Silver perbromide, $AgBr_2$.

"2. Silver subbromide, Ag_2Br or Ag + AgBr.

"3. The original unchanged silver bromide, AgBr.

"On the basis of these results and supported by further experimental data, I attempted finally to give an explanation of the phenomenon of solarization. On a silver bromide gelatine dry plate which had been over-exposed to the point of solarization, I was able to show that the 'indigo image' developed by means of indoxyl is not solarized and that, if the plate is first fixed and then developed physically,

the resulting 'silver image' is also not solarized. In fact both come out as normally graded negatives. From this the conclusion follows directly that the two latent images the 'silver perbromide' one and 'silver subbromide' one were also not solarized. The amounts of the two effective constituents of the latent image—perbromide and subbromide—therefore increases continuously with increasing illumination and no reversal takes place. At first sight it appears paradoxical that the two latent images, when developed together chemically, should give a solarized picture. It becomes intelligible, however, if one reflects that the increase of perbromide and subbromide is necessarily accompanied by a decrease in the amount of the unchanged silver bromide—which last of course furnishes the material from which the silver image is developed. *I look upon this decrease in the supply of silver bromide as the cause of solarization.* With a certain degree of illumination there will be reached a certain equilibrium and the plate will perhaps show the maximum blackening if developed at the stage where there is exactly one molecule of silver subbromide (equal to one atom of 'silver nucleus') to one molecule of silver bromide. If one exposes beyond this stage there is an increase in the amount of silver perbromide and of silver subbromide ('silver nucleus') while the amount of silver bromide decreases. If the plate is developed at this point, the silver nucleus finds less silver bromide to influence than it did at an earlier stage and in consequence the density of the negative must decrease; in other words, there is a reversal of the image.

"Further experiments in this field have shown that, by purely chemical means, solarized images can be obtained from properly exposed non-solarized silver bromide gelatine dry plates. The necessary plates (about 11° to 12° Scheiner) were exposed behind the Chapman-Jones scale photometer for 30 seconds to a paraffin candle at a distance of 305 mm. They were then developed in an indoxyl bath, fixed and washed. If one treats the green negative, thus obtained,

with a potassium cyanide solution, the silver image dissolves, as I have shown before, and there now remains only the pure blue negative indigo picture. This statement as I have since found is only partially accurate and requires the limitation that the plate shall be developed in the indoxyl bath only long enough to produce a negative with plenty of detail, in other words for about 6 to 10 minutes at about 20° C. If one leaves the plate in the indoxyl bath for perhaps half an hour to an hour, the picture gains continually in strength and finally becomes a dark greenish-black. If one then fixes the plate and puts it in the potassium cyanide bath, the indigo image remains behind as a beautiful *solarization negative.* The scale fields from 1 to 10 appear to be solarized, while the others, up to about 22, come out as a blue indigo negative with normal gradations.

"It was not difficult to find an explanation for this *apparent solarization*; it turned out that finely divided silver in a potassium cyanide solution was able to reduce indigo, *i. e.*, to dissolve it as indigo-white. If one places finely-divided indigo and molecular silver in a test-tube, adds a twenty percent potassium cyanide solution, and heats slightly, after a while a portion of the indigo goes into solution as indigo-white. If the solution is now filtered, a clear, light yellow solution is obtained from which air quickly precipitates clots of indigo again. The same process obviously takes place when one treats with potassium cyanide solution a negative which has been developed much too long in an indoxyl bath. The 'silver image' dissolves the 'indigo-image.' When the amount of silver is the greatest the action lasts the longest, *i. e.*, at the points where the illumination has been strongest

"On the other hand, if one fixes and washes a plate which has been developed for an excessive length of time in an indoxyl bath, and then puts the plate into a potassium cyanide bath to which a little potassium ferricyanide has been added, this oxidizing agent contracts the reducing action of the silver. The "silver image" dissolves very rapidly

and there is left a non-solarized indigo negative with normal gradations. If this treatment is given to these plates which have been exposed for an equal length but which have been developed in the same indoxyl bath, one for ten minutes, another for thirty minutes, and the third for an hour, the result is three indigo negatives of exactly the same strength and gradation. From this it follows that the prolonged action of the indoxyl developer intensifies the silver image only and not the indigo image. This is perfectly intelligible in view of what has been said in regard to the nature of the latent image and the process of development."

In Part II, I intend to take up the work of Nipher, Wood and Lugzin. There is also an important paper by Lüppo-Cramer to be considered, to say nothing of the recent work of Trivelli. After that I hope to show the usefulness of the theory of Grotthuss.

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NEW BOOKS

Determination of Radicles in Carbon Compounds. *By H. Meyer and J. Bishop Tingle. Third edition, revised. 13 x 19 cm; pp. xii + 218. New York: John Wiley and Sons; London: Chapman and Hall, 1908. Price: $1.25 net.*—The new matter has been added as an appendix, almost all of the text of the second edition having been retained. In the appendix we find: methods of acetylation; isolation of acetyl derivatives; determination of acetyl groups; benzoyl derivatives; analysis of benzoyl derivatives; acylation by means of other acid radicles; alkylation of hydroxyl groups; preparation and reaction of diphenylcarbonyl chloride; action of phenyl carbimide; determination of hydroxyl by means of alkylmagnesium halides; determination of methoxyl; determination of carboxyl; determination of carbonyl; determination of carbonyl derivatives by hydrolysis; determination of the propenyl group; determination of the ethylene group in amines; determination of the aliphatic amino group; determination of the aromatic amino group; separation of primary and secondary amines by acylating agents; determination of the amido group; determination of the imino group; determination of methylimine; determination of the nitro group; determination of the nitroso group; determination of the azo group; the iodine number; miscellaneous methods.

Since the new portion is more than a quarter of the whole book, it is easy to see that this is a new edition in fact as well as in name. Numerous cross references serve to bind the text and the appendix together.

Wilder D. Bancroft.

De la Méthode dans les Sciences. *By H. Bouasse, Pierre Delbet, E. Durkheim, A. Job, F. Le Dantec, L. Lévy-Bruhl, G. Monod, P. Painlevé, Émile Picard, Th. Ribot, J. Tannery, P. F. Thomas. 12 × 19 cm; pp. iii + 411. Paris: Félix Alcan, Éditeur, 1909.*—This volume contains a series of essays on the different sciences each written by a man prominent in that science. The authors are Jules Tannery for pure mathematics, H. Bouasse for general physics, A. Job for chemistry. A. Giord for morphology, F. Le Dantec for physiology, Pierre Delbet for medicine, Th. Ribot for psychology, E. Durkheim for sociology and the social sciences, L. Lévy-Bruhl for ethics, G. Monod for history, P. Painlevé for mechanics, and Émile Picard for science in general.

The essays are distinctly interesting as the following extracts will show. In the essay on physics, p. 76, we read that "physics seeks to reconstruct its portion of the world by deducing it in a purely syllogistic way from one general principle previously admitted." On p. 93 there is a discussion of the demonstration of principles.

"*Principles are not demonstrated.* It is ridiculous and sad that one should be compelled to enunciate such truisms; but if the reader opens some books on thermodynamics, he will find such titles as: Demonstration of the Principle of Equivalence; Demonstration of the Principle of Carnot. Worse than that, one famous scientific man has claimed to give a demonstration of the principle of virtual work. If we stop a moment to think, we shall see the absurdity of such a thing or at any rate the absurdity of such language.

"The *principle*, *postulate*, or *hypothesis* (the three terms are absolutely equivalent) is that which we take as the first proposition of the sorites. To demonstrate a postulate *theoretically*, is to deduce it from a more evident proposition, which is a contradiction in terms. *We do not demonstrate a postulate; we change a postulate.*

"As for demonstrating a principle *experimentally*, that is an undertaking which is obviously absurd. We may demonstrate that certain facts, or even that all the known facts, fall within a certain form and are consequently contained in the principle underlying this form. Obviously, however, we cannot demonstrate that facts of which we are ignorant also fall within this form."

The final paragraph in the essay on chemistry, p. 147, runs something as follows:

"The fundamental fact from which we started is that of the chemical compound. To find the state of these chemical compounds and the laws governing their changes, is the object which gives chemistry its definite character and its distinctive methods. Actually it attempts to explain the compounds as groupings of atoms and the changes as conversions of energy. Is this a permanent conception? No one thinks so; but the question is premature because we do not even know how to connect the first explanation to the second, how to refer the energy to the atoms. Chemistry can perhaps best be considered just as it is, in the form in which it is developing. It appears certain that a long future is assured to it and a fruitful development, especially if it makes use of physics as an instrument and a guide, and seeks in biology its application and its model."

Wilder D. Bancroft

Handbuch der anorganischen Chemie. *Heraugsgegeben von R. Abegg. In vier Bänden. Dritter Band, dritte Abteilung. 18 × 25 cm; pp. xiv + 876. Leipzig: S. Hirzel, 1907.*—This volume contains chapters on nitrogen (v. Braun), ammonium salts (Pick), phosphorus (Schenck), arsenic (Schenck), antimony (Schenck), bismuth (Hetz), vanadium (Chilesotti) while Brauner has written the chapters on the atomic weights and Lottermoser those on colloids. The most interesting sections of the book are naturally those dealing with nitrogen, phosphorus, and vanadium because these are to most people the more interesting elements. The literature references are surprisingly complete and include the work of Dennis and Miss Isham on hydronitric acid, Cohen's work on explosive antimony and v. Bolton's work on tantalum. The discussion of the oxidation of phosphorus is very good indeed, but it is certainly a mistake to say that phosphorus is made commercially in an arc furnace. It is generally believed that the furnace in commercial use is a resistance furnace, the current passing through the fused charge. Under the catalytic action of vanadium the reviewer did not find the conversion of hypochlorites into chlorates though it may perhaps be there. Like the other volumes of the series this is an invaluable reference book and the set will undoubtedly find a place in every library. *Wilder D. Bancroft*

OSMOTIC STUDIES

(Reply to Ernst Cohen and J. W. Commelin)

BY LOUIS KAHLENBERG

Two years ago I presented in the pages of this Journal[1] an article entitled "On the Nature of the Process of Osmosis and Osmotic Pressure with Observations Concerning Dialysis," in which the results of an extensive series of experimental investigations of both qualitative and quantitative nature were detailed. As the outcome of this work, it was shown that whether osmosis will take place or not in a given case depends upon the specific nature of the septum employed and the liquids that bathe it; and if osmosis does occur, these factors also determine the direction of the main current and the magnitude of the pressure developed. The motive force in osmotic processes lies in the specific attractions or affinities between the liquids used, and also those between the latter and the septum employed. It was furthermore emphasized that osmotic pressures are equilibrium pressures, and that in osmotic processes there is always a current in both directions, though the main current may in specific cases be so much stronger than the minor, that the latter sinks almost into insignificance. In such cases the septum is termed "semipermeable." Vulcanized caoutchouc was found to be a "semipermeable" membrane when it separates pyridine solutions of either silver nitrate, lithium chloride or cane sugar from the pure solvent. The necessity of stirring the contents of the osmotic cell and also the outer liquid during the osmotic pressure measurements was pointed out, and a new apparatus for measuring osmotic pressures accordingly was devised. The results of the osmotic pressure measurements showed that the gas laws do not hold for the solutions studied, and it was consequently pointed out

[1] Jour. Phys. Chem., 10, 141–209 (1906); also Trans. Wisconsin Academy of Sciences, Arts and Letters, Vol. 15, Part 1.

that these laws cannot serve as a basis for a satisfactory theory of solutions.

Immediately after the appearance of this paper Ernst Cohen, director of the van't Hoff laboratory at Utrecht, apparently alarmed at the danger threatening the van't Hoff theory of solutions, published a short notice in the *Chemisch Weekblad*[1] cautioning the public to accept with reserve what he chose to term my far-reaching conclusions. In this note he omits consideration of all my work except the quantitative measurements of osmotic pressures made with solutions of sugar, lithium chloride, and silver nitrate in pyridine, employing a vulcanized caoutchouc membrane, and using pure pyridine as the outer liquid. It will be recalled that the osmotic pressures measured in these cases are far below those calculated according to the gas laws. Mr. Cohen calls attention in his article to the well-known facts that cane sugar may act as a weak acid, that pyridine is a base, that silver nitrate forms addition products with pyridine, and adds that the latter might also act on lithium chloride. In this connection the reference that Mr. Cohen makes to his own work and that of Kullgren in 1901 as demonstrating that cane sugar has weak acidic properties is quite superfluous, for the existence of sucrates, like the sucrate of lime for instance, has been known for a long time. That cane sugar does not form an addition product with pyridine was shown in this laboratory by G. M. Wilcox.[2] Furthermore, that silver nitrate forms with pyridine the compounds $AgNO_3 \cdot 6C_5H_5N$, $AgNO_3 \cdot 3C_5H_5N$ and $AgNO_3 \cdot 2C_5H_5N$ has recently been further investigated here[3] in connection with a study of the equilibrium in the system silver nitrate pyridine. Again, according to researches made in this laboratory,[4] lithium chloride forms with pyridine the compounds

[1] Chemisch Weekblad, Amsterdam, **3**, 290 (1906).

[2] Jour. Phys. Chem., **5**, 589 (1901).

[3] Kahlenberg and Brewer: Jour. Phys. Chem., **12**, 283–289 (1908).

[4] Kahlenberg and Krauskopf: Jour. Am. Chem. Soc., **30**, 1104–1115 (1908).

$LiCl.2C_5H_5N$ and $LiCl.C_5H_5N$. It is, of course, perfectly clear that even if the existence of such addition products in the solutions be assumed, this would not alter the number of dissolved molecules contained in a given volume of solution, though it would increase the size of the dissolved molecule and diminish the number of molecules of solvent accordingly. In solutions like eighth-normal, however, the relative number of solute and solvent molecules would vary but slightly. It is quite evident that the osmotic pressures I observed in the case of the solutions of cane sugar, lithium chloride, and silver nitrate cannot be harmonized with the gas laws by making use of the fact that the last two compounds mentioned are capable of forming addition products with pyridine as above detailed.

This Mr. Cohen appears to have recognized himself, for in his next article, which he published jointly with J. W. Commelin,[1] no explanations of observed osmotic pressures are made on the basis of such possible interactions of solvent and solute.

The fifty-two pages of the paper of Cohen and Commelin present: an introduction of two pages; a review of previous work done in measuring osmotic pressures covering twenty-six pages, of which about eleven pages are devoted to a consideration of my quantitative measurements of osmotic pressure; a description of the authors' own apparatus, methods and preparations used, occupying sixteen pages; three pages devoted to the results of their own measurements; four pages on the influence of water; and finally about half a page giving the summation of the conclusions reached.

The brief introduction is intended to impress upon the mind of the reader the great importance of the van't Hoff theory of dilute solutions, and to duly caution all not to pronounce against that theory "auf Grund einer geringen Anzahl unter sich wenig übereinstimmender Versuche." It is stated that Pfeffer's osmotic pressure measurements are

[1] Zeit. phys. Chem., **64**, 1–52 (1908).

simply used by van't Hoff as corroborations of his computations, and that the real basis of the latter's theory lies not in the osmotic pressure measurements, but rather in the determination of those magnitudes that of necessity are quantitatively related to osmotic pressure, namely: (*a*) isotonic coefficients; (*b*) lowering of the freezing point; (*c*) lowering of the vapor tension; (*d*) elevation of the boiling point; (*e*) change of solubility of gases with pressure; (*f*) partition coefficients. Then follows the remarkable statement that the large amount of material that has been gathered concerning the constants just mentioned would be worthless to him alone, who denies that these are necessarily related to osmotic pressure. This position I would regard as absurd and quite untenable in the light of experimental facts to which I have called attention in my paper. No one would deny the value of the constants above mentioned under (*a*) to (*f*), but it must be denied that they are of necessity related to actual osmotic pressures (that is, pressures that are experimentally measured by means of so-called semipermeable membranes) in any such way as required by the theory of solutions of van't Hoff. I submit that I have shown conclusively by the numerous qualitative experiments (which Mr. Cohen apparently disdains even to discuss) that the specific nature of the membrane and the liquids that bathe it determines whether osmosis will take place or not, and in what direction. It is shown in that paper how to proceed to find substances for which vulcanized caoutchouc is "semipermeable," and it is definitely established upon an experimental basis that the "semipermeability" of a membrane depends upon its selective action. Later in their paper (p. 27) Cohen and Commelin graciously concede that the discovery of vulcanized caoutchouc as a "semipermeable" membrane is of importance as it opens the way to find additional septa of this kind, but they entirely underrate the vastly more important point, that there is really no such thing as a semipermeable membrane, that *osmosis always goes on in both directions, if at all, and that it is only in the few limiting cases when the osmosis*

in one direction by far outweighs that in the other, that we have a so-called semipermeable membrane. A clear recognition of this robs direct osmotic pressure measurements of practically all the importance that has hitherto been accorded them as a foundation for a theory of solutions. On page 27 Cohen and Commelin unearth the following from the reply of van't Hoff[1] to Lothar Meyer: "Wiederum haben wir die im Grunde zwecklose Frage: Was übt den osmotischen Druck aus? Wirklich, wie schon betont, ich kümmere mich schliesslich nur um dessen Grösse; da er sich mit dem Gasdruck gleich gezeigt hat, ist man geneigt, an einen ähnlichen Mechanismus wie bei Gasen beim Zustandekommen zu denken. Wen dies aber auf falsche Wege führt der lasse den Gedanken an Mechanismus einfach fort." Again in this connection they cite from van't Hoff's Vorlesungen:[2] "Es sei betont, dass jede Vorstellung den man sich über den Mechanismus des Entstehens vom osmotischen Drucke oder der Wirkung der semipermeablen Membran macht, ohne Einfluss auf die weitere Entwicklung ist. Die Frage also, ob der Druck vom gelösten Stoff herrührt, kann ganz ausser Spiel bleiben; ebenso diejenige, ob derselbe auf Stoss oder Anziehung begründet ist. Auch die Wirkung der Membran, es sei als Sieb, es sei durch vorübergehende Absorption ist einerlei." As ardent defenders of the van't Hoff ideas they boldly declare on p. 27: "Diejenigen die es sich zur Aufgabe machen, van't Hoff's Auffassung über den osmotischen Druck zu bestreiten, kämpfen gegen Windmühlen;" and on p. 2 of the introduction they state that the time for countenancing the contention that the osmotic pressure is not of necessity related to the constants (*a*) to (*f*) above mentioned, "wäre aber erst dann gekommen, wenn der Versuch gemacht würde, die für jeden Spezialfall auf thermodynamischer Basis fussenden Beweise zu widerlegen."

It is a well-known dodge of the thermodynamicists to

[1] Zeit. phys. Chem., 6, 485 (1892).

[2] Vorlesungen Ueber theoretische und physikalische Chemie, Braunschweig (1899), 2 Heft, S. 24.

claim that they are not concerned with the mechanism of osmosis and with that which produces osmotic pressure, for they simply require to know the magnitude of the latter in order to proceed with their computations. Right here lies the strength, but also the great weakness of thermodynamic methods. *What we want to know above all things is what causes osmosis and osmotic pressure in order to put us into position to discuss more intelligently the results of osmotic experiments, and to determine to what extent such results are actually useful in forming a true basis for a tenable theory of solutions.* But in any case, the thermodynamicists *are* concerned with the magnitude of osmotic pressure when so-called semipermeable membranes are employed. We note with what haste they lay hold of such results as those obtained with aqueous sugar solutions and copper ferrocyanide membranes by Morse and Frazer, which show an approximate agreement with the requirements of the gas laws, and how they pass lightly over the results of Berkeley and Hartley, who obtained much higher pressures than the gas laws require. It is consequently of importance to them that my own work with vulcanized caoutchouc membranes has yielded results that are entirely out of harmony with the gas laws.

Now while with aqueous solutions and a copper ferrocyanide membrane osmotic pressures may apparently in a number of cases, like cane sugar, glucose, amygdaline, antipyrine, salicine and mannite, be obtained which approximate to the requirements of the gas laws; it is equally true, that when we use other membranes and other solutions, osmotic pressures may be obtained that do not conform to the requirements of the gas laws at all. Indeed it would seem probable that the results obtained with cane sugar solutions and copper ferrocyanide membranes are rather a curious exception than an example of the usual osmotic behavior of substances. The "osmotic pressure" as usually used in thermodynamical computations concerning solutions is an hypothetical magnitude which has no counterpart in actual

osmotic phenomena, for the pressure is assumed to be quite independent of the nature of the membrane as long as the latter is "semipermeable," and experiment shows conclusively that this assumption cannot possibly be maintained.

The sixteen pages which Cohen and Commelin devote to a review of osmotic pressure measurements contain facts well known to all and consequently need no further consideration here.

In the eleven pages devoted to a discussion of my paper, Cohen and Commelin describe the method of experimental investigation adopted by me and seek to show that the results of my experiments do not warrant the conclusion that the osmotic pressures observed do not follow the gas laws. Furthermore, they try to make out that my results show that whether the contents of the osmometer and the outer liquid are stirred or not does not affect the osmotic pressure. In their discussion of my results they present three tables in which the numerical data I have collected experimentally are used. These tables are here reproduced and numbered as in their article.

TABLE 3

No. of experiment	Solute	Concentration	Temperature	Osmotic pressure
19	$AgNO_3$	0.1 normal	17°	28.5 cm
20	"	0.05 normal	17°	0.5 "
21	"	normal	—16°	15.6 "
22	"	normal	20°	14.95 atm.
23	cane sugar	0.02 normal	—	22.7 cm
25	"	0.0035 normal	22°.5	5 "
26	"	0.125 normal	0°	1.9 "
27	"	0.25 normal	—16°	17.5 "
28	LiCl	saturated	—	Pressure not given

Except in Experiment 22, the pressures are represented in centimeters of the particular solution employed. In Experiment 22, a closed mercury manometer was used, the mercury being of course in contact with the solution of silver nitrate in pyridine. To this Cohen and Commelin object,

calling attention to the fact that thus silver amalgam forms at the point of contact. While there is an interaction where the mercury touches the silver nitrate pyridine solution, this is slight for the cross-section of the manometer tube is small and the action goes on very slowly; furthermore, in the interaction the equivalent solute content of the solution remains the same. I should like further to call attention to the fact that in my paper I distinctly make the following statement in connection with Experiment 22 (l. c., p. 164): "No special significance will be attached to the single result recorded here, it being given simply to show that a very considerable pressure may be produced by a normal solution of silver nitrate in pyridine when it is separated from pure pyridine by vulcanized caoutchouc at 20°, whereas at —16° (No. 21) the pressure formed is practically insignificant." By means of the remark that in No. 22 silver amalgam is formed, Cohen and Commelin apparently seek to divert the reader's attention from the main issue, for they state in this connection: "Bereits in den in obiger tabellarischer Uebersicht zusammengestellten qualitativen Versuchen glaubt Kahlenberg, den überzeugenden Beweis erblicken zu dürfen für den Satz, dass die Gesetze verdünnter Gase hier nicht gelten;" and then they cite the following from my paper: "Though Experiments 19 to 22 are only quasi quantitative in character, they are already sufficient to show that here the osmotic pressure does not follow the gas laws at all." Now I submit that this latter conclusion is correct, and is precisely the one that any unbiased mind will reach on carefully regarding the data compiled in Table 3, in spite of the opinion of Cohen and Commelin to the contrary.

Cohen and Commelin further present the following compilation of the data that I have collected:

TABLE 4
Experiments without stirring

No. of experiment	Solute	Concentration	Temperature	Osmotic pressure in cm Hg
53*a*	cane sugar	0.25 norm.	17°.5	186.2
			0°.0	125.0
			16°.4	159.5
			17°.5	186.0
53*b*	"	0.25 norm.	17°.5	155.6
			16°.4	166.4
			16°.0	166.7
53*c*	"	0.25 norm.	17°.5	107.4
54*a*	"	0.125 norm.	17°.5	62.4
			0°.0	0.2
			0°.0	0.6 (8 hrs. later)
			14°.5	48.8
			17°.5	62.0
			18°.0	43.6
54*b*	"	0.125 norm.	17°.5	52.8
			14°.5	42.5
			18°.0	46.3
55	"	0.25[1] norm. / 0.125 norm.	16°.8	137.5
56*a*[2]	"	0.25 norm.	22°.0	43.0
56*b*[2]	"	0.25 norm.	22°.0	39.5

TABLE 5
Experiments with stirring

No. of experiment	Solute	Concentration	Temperature	Osmotic pressure in cm Hg
57	LiCl	0.125 norm.	19°.0	51.2
58	"	0.125 norm.	21°.96	54.9
			2°.0	9.0
			21°.4	56.1
			1°.6	2.9
			20°.5	53.0
			36°.0	101.0
			58°.7	128.3
			25°.5	51.9
59	cane sugar	0.125 norm.	20°.0	98.3
60	"	0.125 norm.	22°.15	95.5
			2°.0	±0.0
			46°.0	114.2

[1] The inner liquid was 0.25 normal, while the outer liquid consisted of a 0.125 normal solution.

[2] In No. 56, thick rubber membranes were used.

Now Cohen and Commelin propose to discuss the data in Tables 4 and 5 to ascertain whether these results show that stirring the liquids in contact with the membrane is necessary in osmotic pressure measurements. They say: "Zur Beantwortung dieser Frage wollen wir die Abweichungen vom Mittel in Parallelversuchen berechnen (Tabelle 6)." They present the following table, which, as will be noted, is compiled from Tables 4 and 5:

TABLE 6

No. of experiment		Mode of experiment	Maximum pressure	Mean pressure	Deviation from mean. Percent
I	53*a*	Without stirring	186.0	153.4	21.0
	53*b*	" "	166.7		9.0
	53*c*	" "	107.4		—30.0
II	54*a*	" "	62.4	57.6	8
	54*b*	" "	52.8		
III	56*a*	" "	43.0	41.2	4
	56*b*	" "	39.5		
IV	57	With stirring	51.2	53.0	3.5
	58	" "	54.9		
V	59	" "	98.3	96.9	1.5
	60	" "	95.5		
VI	54*a*	Without stirring	62.4	77.2	—19
	54*b*	" "	52.8		—32
	59	With stirring	98.3		27
	60	" "	95.5		24

Concerning Table 6, Cohen and Commelin then continue as follows: "Aus Tabelle 6 ergibt sich nun Folgendes: 1. Dass die Abweichungen in Parallelversuchen, die ohne Rühren ausgeführt werden (III) nicht grösser zu sein brauchen, als in Parallelversuchen mit Rühren (IV), so dass der Einfluss des Rührens hier gar nicht bewiesen ist. 2. Dass die Abweichungen zwischen vergleichbaren Versuchen, die einerseits mit Rühren, anderseits ohne Rühren ausgeführt sind, nicht grösser sind als die, welche vorkommen können in Versuchen, die alle ohne Rühren (I) ausgeführt wurden. Es

scheint uns demnach wenig konsequent, wenn Kahlenberg diese Abweichungen in den zwei Fällen auf Rechnung entgegengesetzter Ursachen bringt und sie in (I) einer ungenügenden Mischung der verschiedenen Flüssigkeitsschichten im Osmometer zuschreibt, in (VI) aber einer durch Rühren verbesserten Durchmischung. Streng genommen ist hiermit schon nachgewiesen, dass Kahlenberg nicht das Recht hatte, die Ergebnisse der vier Versuche 57–60 (denn nach seiner eignen Aussage sind nur diese als entscheiden zu betrachten) als ein genügendes Argument zu betrachten für seinen Schluss, dass die einfachen Gasgesetze nicht für verdünnte Losungen gelten. Er scheint dann auch, vielleicht ganz unbewusst, die Schwäche seiner Beweisführung selbst gefühlt zu haben. Denn obwohl er sich einerseits, wie wir gesehen haben, sehr kategorisch über den Wert aller früheren Versuche die ohne Rühren ausgeführt wurden, äussert, zaudert er nicht, an mehreren Stellen seiner betreffenden Abhandlung selbst qualitative Versuche wie Nr. 20 und 25 (Tabelle 3) zur Stütze seiner Darlegungen heranzuziehen." I have quoted Cohen and Commelin thus in full, in order that their exact attitude may be understood and no injustice be done them in pointing out the fallacy of their position.

In the first place (I) in Table 6 represents an early set of results obtained with a 0.25 normal sugar solution, whereas all the other results with sugar solutions in Table 6 were obtained with solutions of half that strength. Results in (I) can consequently not be compared with others of the table. Again, results (III) in Table 6 were obtained with a thick rubber membrane of entirely different quality than that used in the other experiments detailed in the table, consequently group (III) is not comparable with the other results. Now again, Experiments 57 and 58, namely Group IV, Table 6, were conducted with lithium chloride as solute, whereas all the others in the table were carried out with sugar as solute; the results of Group IV are consequently not to be compared with the others in Table 6. We have left then solely for legitimate comparison Groups II and V of Table 6, which

are gathered in Group VI, Table 6. It will be noted on looking at Table 6, Group VI, that the results without stirring are *very* much lower than those with stirring, the former being less than two-thirds of the value of the latter. Now Cohen and Commelin take the mean of the results with and without stirring in Group VI and compute (in the last column of the table) the deviation from this mean and compare these deviations from the mean with those of Group I, with which, as stated above, they are not comparable at all. Moreover, *the argument that stirring is necessary in quantitative osmotic pressure measurements is not that fairly concordant results might not be obtained without stirring*, as Cohen and Commelin seem to think, but rather that, *in carefully executed, perfectly comparable experiments, stirring always yields higher pressures.*

Any one comparing the results I have obtained with stirring and without stirring in the case of the 0.125 normal sugar solutions (Nos. 54*a* and 54*b* with 59 and 60) must certainly admit that stirring greatly increases the osmotic pressure developed. To compute the mean of the results of these four experiments and to argue for the deviation of the individual results on either side of such mean that the effect of stirring is nil is obviously absurd. Nor do I base the fact that it is necessary to stir in seeking to measure maximum osmotic pressures entirely upon the results of Group VI, Table 6, for in numerous other cases after I had accidentally discovered the effect that jarring the apparatus had in increasing the osmotic pressure, I assured myself that after the pressure had apparently become constant, stirring or even shaking would cause the pressure to increase further. I desire to emphasize that I consider this fact quite indisputable, for since the publication of my paper numerous other experiments on osmosis in this laboratory have confirmed this fact, which, moreover, one would naturally expect to find from the considerations laid down in my paper concerning the nature of the process of osmosis.

I have never used Nos. 20 and 25, Table 3, as an argu-

ment in discussing the effect of stirring in osmotic pressure measurements. But I have used and do still use these as a most powerful argument against the contention that the gas laws hold for osmotic pressures of dilute solutions. Moreover, *all the results in Table 3 are an unanswerable argument against the tenet that the gas laws hold in osmotic experiments.* In fact I consider all the qualitative and quasi quantitative experiments that I have made and described in my paper as a powerful argument against the contention that the gas laws regulate osmotic pressure. My references to these qualitative and quasi quantitative experiments are consequently not made because of an unconscious realization of the weakness of the argument presented by the quantitative measurements, as Cohen and Commelin pretend, but rather with the full realization that, as I have stated in my original article, the results in Table 3 "are already quite sufficient to show that here the osmotic pressure does not follow the gas laws at all." The soundness of this position I cheerfully leave to the judgment of others. Indeed, after the publication of my paper, many men of prominence, among them no less a one than the late Professor H. W. Bakhuis-Roozeboom of Amsterdam, expressed themselves to me in writing as to the correctness of my position. We are, moreover, at present engaged in this laboratory in determining the lowest concentrations of various solutions that will still develop an osmotic pressure that is appreciable at all. This work has already yielded an abundance of further results showing that stirring is quite necessary and that the gas laws do not govern here at all. In due time the results of these labors will be published. On account of its nature, the work requires considerable time.

On pages 25 and 26 of their article Cohen and Commelin try to make out that in testing the effect of temperature on osmotic pressure my osmometer acted mainly as a thermometer, that the experiments were not run long enough, and that the reason that the osmotic pressures were found

to be nil[1] at low temperatures was because the membranes were not supported from above and consequently bulged, that is, were convex upward. In answer to this I wish to call attention to the fact that these gentlemen have performed experiments only at 25°, and that consequently what they say might have happened, or did happen, in my experiments at lower temperatures are merely conjectures. It is therefore quite unnecessary to go into the details of their considerations here; suffice it to say, they are entirely untenable; but I wish to state that in no case could there have been any bulging inward of the membrane of my osmometer, for the membrane was always under slight pressure from within outward. Moreover, I wish to call special attention to the fact that the stretched rubber membrane over the mouth of the osmometer does not yield and bulge inward, "beim geringsten Ueberdruck," as Cohen and Commelin state; in fact it takes quite an appreciable pressure to cause such a tense membrane to bulge inward so as to cause a notable effect on the osmometer, of which I have recently assured myself experimentally.

But to settle the whole matter as to whether the 0.125 normal sugar solution actually gives practically no osmotic pressure as found before, I chose the best method, namely renewed experiment. I prepared a 0.125 normal sugar solution and with it performed three independent osmotic experiments at 0°. The substances and the procedure were practically those described in my previous paper. The solution, the pyridine used as outer liquid, and the apparatus were first each separately chilled to 0° by means of ice in a cold cellar, care being taken to guard the liquids and interior of the apparatus from moisture. The osmometers were quickly filled and the apparatus quickly set up. All was done practically at 0° and the apparatus was kept at 0° by means of a large amount of chopped ice. Thus the possibility of ther-

[1] The osmotic pressures at zero and below were by no means always nil as Cohen and Commelin pretend. Compare for instance Table 3, results at 0° and at —16°.

mometric effect was completely eliminated.[1] In two of these experiments (*a* and *b*) the membranes employed were of the same manufacture as those used in my previous quantitative measurements; in the other case (*c*) a thinner vulcanized caoutchouc membrane of excellent quality, but of different manufacture, was employed. In setting up the experiments care was taken to have the level of the liquid in the stem of the simple osmometer employed slightly above that of the outer liquid to begin with, so that there could be no possibility of the membrane becoming convex inward. Moreover, to doubly safeguard that such bulging did not happen, a simple contrivance was introduced into the osmometer, which would indicate any upward convexity of the membrane if it occurred. This contrivance consisted of a small, very light weight, perforated sheet iron disc to which was soldered a long iron wire. The disc rested on about the center of the membrane, and the wire passed upward into the stem of the osmometer, on which by means of a mark the position of the upper end of the wire was sharply located. During the experiments not the slightest inward convexity of the membranes was observed, for the end of the wire, which was slightly bent so as to form a pointer, always rested on the same mark. Mercury manometers were not used, for they were quite unnecessary, the pressures being so slight. In (*a*) and (*b*) the maximum pressures in cm of the osmometer liquid were 7 and 9 cm, respectively, while in (*c*) where a membrane of different quality was used, a maximum pressure of 23 cm was obtained. These pressures developed within the first ten hours, and remained practically constant for about three days. During the fourth day they began to diminish slowly, showing that the maximum had been reached. After four days the experiments were discontinued.

[1] It would seem quite superfluous to add here that thermometric effects were also guarded against in all my previous experiments. Every one who has worked with osmotic apparatus in quantitative osmotic pressure measurements knows that due care must be taken to avoid thermometric effects of the osmometer.

The outer liquids showed the presence of only traces of sugar; the exact amounts were not determined. From these experiments it is evident then that the osmotic pressure of 0.125 normal sugar solutions at 0° is very slight indeed, which practically confirms my previous experiments, No. 54*a* and 60, and demonstrates that the explanations of Cohen and Commelin are untenable. To Mr. W. G. Wilcox, who assisted me in carrying out these experiments, I take this opportunity to extend my thanks.

A careful scrutiny of the various results I have previously obtained at different concentrations and at different temperatures will lead any unbiased person to the conclusion that the gas laws do not regulate the osmotic pressures observed. Moreover, as stated above, we are at present measuring the minimum concentrations at which various solutions show any appreciable osmotic pressure whatever, and this work is being carried on at different temperatures. The results indicate that the osmotic pressures are not governed by the gas laws at all.

Having thus shown that the objections of Cohen and Commelin to my experiments and conclusions are worthless, let us turn our attention to their own attempts to measure osmotic pressures. They chose cane sugar as solute and pyridine as solvent, using a rubber membrane as I did. They seem to have had difficulty in securing good vulcanized caoutchouc, which in America is available at practically every dentist's office. At Mr. Cohen's request I sent him a piece of the rubber I had used. They constructed an apparatus similar to mine, but were unable to get concordant results from similar experiments, without, however, being able to find a reason for such discrepancies. They discuss the possibility that in their experiments the membrane was not thoroughly imbibed with pyridine while being tied on the osmometer, that the tension of the membranes was different in different cases, that the cloth used might have stretched, that the temperature was not the same throughout the apparatus, that the electric stirrer moved through too small a

distance, and that water might have gotten into the apparatus. They then proceed to construct another apparatus calculated to obviate these difficulties. They make the cell of iron; fasten the glass manometer into it with glycerine-litharge cement; put the membrane into place by pressing it unstretched against the flange bottom of the cell, using a large metal ring and bolts. They further cement a glass tube into another iron tube attached to the cell in order to be able to work the electric stirrer, and place the whole cell into another cylindrical glass vessel fitted with a sheet iron cover through which pass a thermometer, the stem of a calcium chloride tube, the stem of a Witt stirrer and the manometer tube. They seek to get all these joints absolutely tight, and then further seek to secure the sheet iron cover to the glass cylinder by attaching to the latter a circular trough of sheet iron, into which the cover is laid and secured by means of a mercury joint, over which, since it is to be used under some pressure, they put a cement consisting of a mixture of pitch and wax. And thus they claim to secure an absolutely tight apparatus which can be completely immersed in the water of a thermostat; to use their own language, "In dieser Weise lässt sich das äussere Gefäss samt Deckel in das Wasser des Thermostaten bringen ohne dass Gefahr besteht, dass auch nur die geringste Spur Wasser in den Apparat dringt." On p. 41 they reiterate practically the same statement. But one looks in vain in their paper as to how they determined that this remarkable apparatus with its many so perfectly made joints was tested to make sure that it could be kept under water for days at a time without having the least trace of water enter into it. The test they used with the bicycle pump to determine whether the inner cell was tight seems to me also quite inadequate. Further, they test the inner and outer liquid with a polariscope, a procedure which might do for the strong solutions used in the osmometer cell, but which is worthless in testing the outer liquid, which is so dilute that in a 50 cm. tube the rotation is only a few hundredths of one degree (see p. 45 of

their paper) and consequently lies almost within the limits of experimental error. It is precisely for this reason that I did not employ a polariscope (which to be sure is, to use their language, "sehr bequem") and took the trouble to evaporate the entire outer liquid to dryness, invert the sugar and determine its amount with Fehling's solution.

Considering now the results of Cohen and Commelin, we find that they are given in their Tables 11 and 14 as follows:

FROM TABLES 11

Concentration	Pressure in cm Hg		Theoretical osmotic pressure from Table 12
	I	II	
0.025 norm.	10.3	6.2	—
0.025 "	17.9	12.3	46.48 cm Hg
0.05 "	34.7	41.2	92.96 " "
0.05 "	35.3	22.5	—
0.10 "	82.3	67.1	185.92 " "
0.10 "	50.8	71.9	—

All work was done at 25° C., and in Table 11 without stirring.

TABLE 14

Membrane	Maximum osmotic pressure in cm Hg at 25°. Solutions are 0.1 normal	
	Without stirring	With stirring
"Cofferdam"	47.8	63.2
	71.7	50.1
From Kahlenberg	65.4	75.6
	54.2	46.4

The values in Table 14 are the only ones obtained without and with stirring.

From Table 11 it appears at once that the results are not concordant in the parallel experiments, which fact Cohen and Commelin also point out, without, however, being able to ascribe a reason therefore. Furthermore, in Table 14

parallel results do not agree, and just half of them are higher with stirring, and the other half are higher without stirring. The authors conclude that they have not measured equilibrium pressures in any of these cases and that the effect of stirring is nil. Cohen and Commelin finally devote four pages to the influence of water in their experiments, surely a timely topic considering the many jointed apparatus they use immersed completely in the water of a thermostat. The experiments with water will not be discussed here, for the authors promise to look into the matter further. They state that the fact that their pyridine boiled between 115° and 117° showed that it contained some water. Now the truth is that the addition of water to pyridine lowers the boiling point; and the high and slightly rising boiling point which dry pyridine shows on distilling it, is due to the presence of slight amounts of higher boiling homologues, notably picoline, which the pyridine contains.

In their final summation, Cohen and Commelin state that their critical study of my experiments shows that I had no right to doubt the validity of the gas laws as applied to osmotic pressures on the basis of my experiments, a position which, as I have pointed out in the present paper, cannot be maintained, for all my experiments show conclusively that the osmotic pressures do not follow the gas laws. And what about the osmotic pressures which Cohen and Commelin themselves present as the results of their own measurements! Are not these all far below what the gas laws require, poorly concordant though they be? And then Cohen and Commelin boldly assert that they have constructed a new apparatus in which the errors attached to my experiments were circumvented. But let any unbiased critic regard the results they have obtained with this "improved" apparatus. I take it that these speak powerfully against the claims they make for it. My osmotic cell and manometer attached were together made of but one piece of glass; there were no cemented joints whatever used in any part of the apparatus. This is to be considered as far superior to the apparatus of

Cohen and Commelin, which contains joints that, as every careful experimenter knows, are well-nigh impossible to secure perfectly. Again, they use a ground glass joint to attach their manometer to the glass tube that is cemented into the cell, as stated above, and they grease this ground glass joint and seek to secure it further by tying it in place with string. It is needless to remind the reader that pyridine is an excellent solvent for grease. Further, by keeping the temperature constant by means of a constant temperature room, instead of immersing the whole apparatus into an aqueous thermostat, I avoided the danger of getting water into the apparatus. Again, whether the membrane is stretched to a somewhat different degree in different experiments or not makes no difference, of which fact I assured myself early in my researches (see p. 190 of my paper). I desire to add here too that whether the membrane is first soaked in pyridine before tying it on or not, makes no difference. In all my experiments the membrane was stretched moderately tight so that no folds were encountered in making the joint between glass and rubber and no wrinkles occurred when the rubber was later soaked in pyridine. The cloth was always tightly stretched on dry, and then when it became wet with pyridine it shrank on still more securely. A yielding of the strong cloth used in the slight pressures measured was not to be feared. The work of Cohen and Commelin of attaching the membrane to the osmometer in the cumbersome way they adopt is quite unnecessary; it is also to be observed that the rubber jammed between the metal ring and the base of their osmometer also acts somewhat in the osmosis, and this part of the membrane is certainly always under different strain in different experiments, for it is obviously quite impossible to tighten the bolts used alike in different experiments. Furthermore, I should like to state here that in my Experiment No. 20 where a steel cell was used, the membrane was attached to the cell in much the same way as that adopted by Cohen and Commelin.

With their apparatus which is thus open to serious ob-

jections, Cohen and Commelin have in two series of experiments made with and without stirring, Table XIV, been unable to confirm the fact that when the experiments are conducted with stirring higher results are always reached; on the other hand, they have also clearly been unable to demonstrate the contrary. The Witt stirrer, which they used, is inefficient; the hollow space under the osmotic cell due to the projection of the heavy iron ring, makes thorough mixing of the outer liquid increasingly difficult. Furthermore, the cloth they use to support the membrane from above by retaining the solution operates greatly against keeping a solution of proper concentration in contact with the upper side of the membrane, which is obviously of prime importance. Again, their inner stirrer had simply a disc at the lower end and no lateral prongs as in my apparatus.

Summary

In summing up the situation then, Cohen and Commelin have failed to show that stirring is unnecessary in measuring maximum osmotic pressures. Their apparatus has failed to yield concordant results and it can consequently not be regarded as an improvement on the one I used, as they claim. If anything, the results Cohen and Commelin present are additional evidence demonstrating that the gas laws do not hold for osmotic pressures in the cases investigated.

In consideration of all the facts presented, there is no reason whatever for modifying the conclusions I have reached in my previous paper.

Laboratory of Physical Chemistry,
University of Wisconsin,
December, 1908

A PRELIMINARY STUDY OF LEAD CHROMATE

BY E. E. FREE

This work was undertaken in the endeavor to determine if possible in what way and to what extent the character of precipitated lead chromate varied with the conditions of precipitation. If satisfactory results were obtained by purely chemical methods it was intended next to study the electrolytic precipitation of lead chromates, the work forming one step in an extended study of the electrolytic precipitation of pigments, which is in progress at Cornell. No work has been done on electrolytic precipitation and only a beginning made on the study of the chemical precipitation. As, however, there is no possibility of my being able to carry the work further, it has seemed desirable to publish the results (obtained in the spring of 1906) in the hope that they may prove interesting and suggestive to other investigators.

I. THE CHROMATES OF LEAD

Neutral Chromate—$PbCrO_4$

The neutral chromate is formed by the reaction of any neutral lead salt with an acid or neutral solution of any chromate or bichromate. It is ordinarily prepared by the precipitation of a lead salt—nitrate or acetate—by potassium chromate, and so formed it is a brilliant yellow, cryptocrystalline powder practically insoluble in water[1] and decomposed by strong acids[2] or alkalis.[3] Weak solutions of alkalis or alkaline carbonates change it more or less completely into one or other of the basic salts.

Lead chromate occurs native as crocoite or crocosite

[1] 0.2 mg. per liter at 18°. Kohlrausch and Rose: Zeit. phys. Chem., **12**, 241 (1893).

[2] Vauquelin: Ann. Chim. Phys. [1], **25**, 196 (1798). Schwartz: Dingl. Polyt. Jour., **186**, 31 (1867). Duvillier: Comptes rendus, **76**, 1353 (1873).

[3] Vauquelin: loc. cit. Brandenburg: Scher. Nord. Ann., **3**, 61 (1819). Rosenfeld: Jour. prakt. Chem. [2], **15**, 239 (1877). Lachaud and Lepierre: Bull. Soc. Chim. Paris [3], **6**, 230–232 (1891).

and was known as such long before its true nature was suspected. In it Vauquelin in 1797 discovered the element chromium. It occurs in transparent orange-red monoclinic prisms with a yellow streak. Artificial crystals of lead chromate are claimed to have been produced by all the following ways:

1. By placing solid potassium chromate and lead nitrate in separate cylinders set in a wide dish and filling the dish with water over the tops of the cylinders.[1] $PbCrO_4.2PbO$ is also obtained.

2. By allowing solutions of a lead salt and a chromate to diffuse into each other through a porous diaphragm.[2]

3. By adding a solution of potassium bichromate drop by drop to a solution of lead nitrate in nitric acid.[3]

4. By placing a lead-platinum couple in a solution of chromic chloride in a sealed tube.[4]

5. By dissolving powdered lead chromate in dilute nitric acid (1/5 to 1/6 full strength) at 100°–150°, filtering, and allowing the solution to cool slowly.[5]

6. By running a slow stream of a solution of lead acetate into a solution of chromic oxide in nitric acid.[6]

7. By heating to fusion a mixture of lead chromate and potassium chromate.[7]

The artificial crystals resemble the natural crocoite in color and other properties.

An unsuccessful attempt was made by the author to produce crystals of $PbCrO_4$ by allowing solutions of potassium chromate and lead nitrate to diffuse together. The solutions were in the arms of a U tube, the bend of which was occupied by a saturated solution of sodium nitrate.

[1] Drevermann: Liebig's Ann., **87**, 120 (1852); **89**, 36 (1853).

[2] Vohl: Ibid., **88**, 114 (1893).

[3] de Schulten: Bull. Soc. Franç. Min., **27**, 129 (1904).

[4] Gmelin-Kraut: Handbuch anorg. Chem., Vol. I, p. 717 (1877). The method is credited to Becquerel.

[5] Bourgeois: Bull. Soc. Chim. Paris [2], **47**, 882 (1887).

[6] Mayer: Ber. chem. Ges., Berlin, **36**, 1743 (1903).

[7] Manross: Liebig's Ann., **82**, 359 (1852).

The clots of lead chromate obtained were composed of microscopic crystals only, and differed in no distinguishable particular from the precipitates prepared in the ordinary manner.

Basic Lead Chromates

The best known basic chromate is the pigment "chrome red"—$PbCrO_4.PbO$ or $2PbO.CrO_3$. It may be made in the following ways:

1. By heating the neutral chromate with solutions of the caustic alkalis or alkaline carbonates[1] or with calcium or barium hydroxide,[2] etc., or even by long contact with these solutions (especially the caustic alkalis).

2. By precipitating the chromate in the presence of free alkali.[3]

3. By dissolving the neutral chromate in solutions of the caustic alkalis and allowing these solutions to evaporate[4] or to slowly absorb carbon dioxide.[5]

4. By combining chromate solutions with basic salts of lead.[6]

5. By boiling PbO[7] or $Pb(OH)_2$[8] or $PbCO_3$[9] or $PbCrO_4$[10] with solutions of potassium chromate, or by boiling $PbCrO_4$ with two-thirds its weight of PbO,[11] or with white lead,[12] or by

[1] Grouvelle: Ann Chim. Phys. [2], **17**, 352 (1821). Weber: Dingl. Polyt. Jour., **279**, 212 (1891). Göbel: Chem. Ztg., **23**, 543 (1899).

[2] Ost: Lehrbuch tech. Chem., p. 476 (1890).

[3] Vauquelin: Ann. Chim. Phys. [1], **70**, 90 (1809). Faraday: Quart. Jour. Sci., **19**, 155 (1825).

[4] Liebig and Wöhler: Pogg. Ann., **21**, 580 (1831). Lechaud and Lepierre: Bull. Soc. Chim. Paris [3], **6**, 230 (1891).

[5] Gmelin: Handbook Inorg. Chem., Watts's Trans., Vol. V, p. 169 (1851). The process is credited to Hayes.

[6] Grouvelle: loc cit., p. 353. Fanzoy: Dingl. Polyt. Jour., **169**, 156 (1863). Weber: loc. cit. Göbel: loc. cit.

[7] Gmelin-Kraut: Handbuch anorg. Chem., Vol. III, p. 279 (1877).

[8] Strömholm: Zeit. anorg. Chem., **38**, 444 (1904).

[9] Dulong: Schweigger's Jour., **5**, 384 (1812). See also Badams: Ann. Phil. N. S., **9**, 303 (1825), and Göbel: loc. cit.

[10] Dulong: loc. cit. Göbel: loc. cit.

[11] Grouvelle: loc. cit. Badams: loc. cit.

[12] Guignet: Fabrication des Couleurs, p. 101 (1888).

heating two parts PbO and one part K_2CrO_4 made into a paste with water.[1]

6. By heating the neutral chromate for some time in contact with molten potassium nitrate[2] or molten sodium chloride.[3]

7. By heating the neutral chromate to redness for some time.[4]

The true chrome red is a dark red crystalline powder. It has, however, been obtained in fine yellowish needles (from KOH)[5] and as an apparently amorphous yellow powder (by heating $PbCrO_4$).[6] These lighter shades may possibly be due to the addition of water,[7] and the formula $PbCrO_4.Pb(OH)_2$ has been suggested for the hydrated compound thus formed.[8] Bodies intermediate in color between the neutral and the basic chromates may also be obtained by rendering the former only partially basic. These are the "chrome orange" pigments and are doubtless mixtures of $PbCrO_4$ and $PbCrO_4.PbO$. They deepen in shade with increase of basicity.

The basic chromate, $2PbCrO_4.PbO$ or $3PbO.2CrO_3$,[9] occurs native as melanochoite or phönicite in dark red tabular

[1] Rosenfeld: Jour. prakt. Chem. [2], **15**, 239 (1877).

[2] Liebig and Wöhler: loc. cit. Fuss: Erdmann's Jour., **18**, 228 (1833). Lachaud and Lepierre: Comptes rendus, **110**, 1035 (1889).

[3] Lachaud and Lepierre: loc. cit.

[4] Marchand: Jour. prakt. Chem., **19**, 65 (1840). Cr_2O_3 is also produced.

[5] Lachaud and Lepierre: Bull. Soc. Chim. Paris [3], **6**, 230 (1891).

[6] Lehmann: Taschenbuch Theor. Chem., 6th Ed., p. 215 (1854).

[7] Guignet: Fabrication des Couleurs, p. 181 (1888). This assumption is strengthened by the fact that melanochoite changes from dark red to lemon-yellow on exposure to the air. Dana: System of Mineralogy, 6th Ed., p. 914 (1892).

[8] Wagner: Chemical Technology, Crookes' Trans., p. 471 (1892). Ost: Lehrbuch tech. Chem., p. 476 (1890).

[9] There is some uncertainty about the composition of this compound. The formula given the text is that favored by Drevermann (loc. cit.), Lachaud and Lepierre (loc. cit.), Dana (System of Mineralogy, 6th Ed., p. 914 (1892)), etc. The formula $PbCrO_4.2PbO$ or $3PbO.CrO_4$ is favored by Gmelin-Kraut (Handbuch anorg. Chem., Vol. III, p. 279 (1877)), and by Moissan (Traité Chim. Min., Vol. IV, p. 1053 (1906)).

crystals with a brick-red streak. It has been produced artificially in the following ways:

1. Together with $PbCrO_4$, by the slow mixing by diffusion of solutions of potassium chromate and lead nitrate.[1]

2. By electrolysis through a connecting capillary tube of solutions of potassium bichromate and potassium plumbate.[2]

3. By heating the neutral chromate at a red heat for two hours in contact with molten sodium chloride.[3]

4. By the action of a solution of potassium bichromate on galena.[4]

Two other basic chromates have been prepared: $Pb_4Cr_5O_{16}$,[5] and $4PbO.CrO_3.H_2O$;[6] and still another has been found native in South Africa.[7]

Lead Dichromate—$PbCr_2O_7$

The previous long-continued doubt[8] as to the existence of a dichromate of lead has been recently resolved by Cox[9] who has shown by phase-rule methods that it does exist, and is stable in contact with solutions containing at least 6.87 gram-molecules of CrO_3 per liter. In contact with solutions of less concentration it is changed to the neutral chromate. It is a brick-red crystalline-powder.

II. THE COLORS OF THE LEAD CHROMATES

As the lead chromates are used principally for pigments their color is of great importance and much attention has

[1] Drevermann: Liebig's Ann., **87**, 120 (1852); **89**, 11 (1853). See p. 2. of this paper.

[2] Becquerel: Comptes rendus, **79**, 85 (1874).

[3] Manross: Liebig's Ann., **82**, 359 (1852). Lachaud and Lepierre: Bull. Soc. Chim. Paris [3], **6**, 230 (1891).

[4] Meunier: Comptes rendus, **87**, 656 (1878).

[5] Moissan: Traité Chim. Mineral, Vol. IV, p. 1053 (1906).

[6] Strömholm: Zeit. anorg. Chem., **38**, 443 (1904).

[7] $4PbO.3CrO_3$, Dawson, Mineralogical Mag., **6**, xviii (1885).

[8] Its existence had been affirmed by Preis and Rayman (Ber. chem. Ges. Berlin, **13**, 343 (1880)) and Mayer (Ibid., **36**, 1743 (1903)) and denied by Schulernd (Jour. prakt. Chem. [2], **19**, 38 (1879)), Lachaud and Lepierre (Bull. Soc. Chim. Paris [3], **6**, 231 (1891)), and Autenrieth (Ber. chem. Ges. Berlin, **35**, 2063 (1902)).

[9] Jour. Am. Chem. Soc., **28**, 1701 (1903).

been given by investigators and manufacturers to processes and conditions of preparation which increase the purity and clarity of the color. Especially is this the case with chrome yellow and there have been proposed a large number of mutually contradictory methods, for each of which is claimed the supremacy in the production of good pigmentary material. It is neither possible nor desirable to enter into a detailed discussion of these processes, but it may be interesting to indicate certain facts which are conceded by all or nearly all investigators, and certain lines of suggestion which are especially important.

Basicity and Color

It is evident from the first part of this paper that the effect of increasing the basicity of the normal chromate is to "deepen" the color and displace the maximum spectral intensity toward the red. By, therefore, preparing a series of bodies of varying basicity—which means probably varying relative quantities of $PbCrO_4$ and $PbCrO_4.PbO$—it is possible to obtain an unbroken series of colors varying from the pure yellow of the neutral chromate to the deep orange-red of the pure basic compound. The colors of the other basic chromates do not differ materially from that of $PbCrO_4.PbO$—the variations among different samples of the same compound often being greater than the differences between the compounds. These variations in the color of the same compound are rather puzzling, as are also the yellow basic compounds already mentioned, or the transient violet compounds of apparently greater basicity which have been observed by Prinvault.[1] They may be due to variations in basicity, hydration, etc., or to differences in the average size of the component crystals, as will be noted below. Excluding these exceptions increase of basicity always means darkening and reddening of the color and for the production of clear yellows it is therefore essential that the formation of basic salt be so far as possible avoided.

[1] Dingl. Polyt. Jour., 220, 259 (1875).

This matter is of considerable practical importance and especially so on account of the extreme readiness with which the neutral chromate becomes basic during the process of preparation. The slightest trace of alkali,[1] a temperature somewhat higher than usual,[2] and probably many other unknown causes will suffice to give to the resultant precipitate a darker or "dirtier" color. This phenomenon—technically known as "turning"[3]—is the cause of frequent loss to manufacturers of colors as the material thus affected is usually quite useless for pigment.

It is possible, as will appear below, that turning is sometimes due to other and totally distinct causes, but in most cases it is doubtless the visible sign of a partial change of the chromate to the basic condition.[4] This seems especially plausible in the light of the well-known fact that the presence of small amounts of free acid in the solution reduces the occurrence of turning to a minimum.[5] An excess of the chromate in the precipitating solutions seems to favor the occurrence of turning and an excess of lead to inhibit it.[6]

[1] Vauquelin: Ann. Chim. Phys. [1], **70**, 90 (1809). Thenard: Chimie, Vol. III, p. 533 (1834). Berzelius: Traité de Chimie, 2nd Ed., Vol. IV, p. 109 (1847); etc.

[2] Vauquelin: loc. cit. Anthon: Repertorium Pharm., **76**, 129 (1842). Guignet: Fabrication des Couleurs, p. 101 (1888). Dammer, Handbuch chem. Tech., Vol. IV, p. 564 (1898); etc. Anthon thinks that the lighter color of precipitates made in the cold is due to hydration.

[3] Preparations of chromate occasionally "turn" some time after the precipitation is completed. This is probably due to the presence of alkali in the precipitate. Grouvelle found determinable amounts of alkali in several orange-colored chromates (Ann. Chim. Phys. [2], **17**, 353 (1821)).

[4] See the extended investigation of turning by Dullo: Deutsche Illustr. Gewerbezeitung, **30**, 272 (1865).

[5] Godon: Ann. Chim. Phys. [1], **53**, 226 (1805). Vauquelin: loc. cit. Dumas: Traité Chim. Appliquée, Vol. IV, p. 584 (1831). Hofmann: Chemische Industrie, Vol. II, p. 730 (1875). Weber: Dingl. Polyt. Jour., **279**, 212 (1891). Wagner: Chemical Technology, p. 471 (1892).

[6] Weber: Jour. Soc. Chem. Ind., **4**, 671 (1885); **10**, 710 (1891). Dammer: Handbuch Chem. Tech., Vol. IV, p. 564 (1898). Hurst: Painter's Colors, 3rd Ed., p. 128 (1901). Thorp: Industrial Chem., p. 218 (1905). Dullo (loc. cit.) dissents from this position.

Color and Crystal Size

The color difference between crystallized lead chromate and the powdered compound is very marked. Natural crocoite is a deep orange and the artificial crystals are of the same color. The contrast with the ordinary brilliant yellow powder is very striking. This difference seems entirely due to the difference in size of particle, for when crocoite is finely powdered (as for instance in taking the streak) it shows a yellow scarcely less brilliant than that of the precipitated compound. The behavior of the basic chromates is quite analogous—the larger crystals corresponding to the deeper and redder shades.[1] When chrome red is ground it takes on a decided yellow tinge.[2] The streak of the dark melanochoite is a brick-red.[3] Chromates prepared by the action of chromate solutions on lead hydroxide are redder when the hydroxide is crystalline.[4]

This behavior of pigments on grinding is probably to be explained as the effect of the light reflected from the external surfaces of the crystals in the ground powder. "The reflection spectrum of pigments arises from two distinct sources: (*a*) light reflected from the surface of the substance; (*b*) light reflected from the interior faces. The light reflected from the surface is nearly white. * * * * It is to the light internally reflected that the pigment owes its color."[5] The colored light reflected from a layer of pigment is that part of the incident light which has entered at least one of the crystals and been reflected from the posterior surface of that crystal, or from the surface of some other crystal situated more deeply within the mass. The colored light is, as above quoted, light reflected from "interior faces."

[1] Habich: Dingl. Polyt. Jour., **140**, 126 (1856). Göbel: Chem. Ztg., **23**, 544 (1899). Bersch: Manufacture of Mineral and Lake Pigments, p. 186 (1901).

[2] Fuss: Erdmann's Jour., **18**, 230 (1833).

[3] Dana, System of Mineralogy, 6th Ed., p. 914 (1892).

[4] Redlich, German Patent, 117,148, Jan. 16, 1901; see Chem. Zent., **1901**, **1**, 288. It is possible that this may be an effect of a higher basicity of the crystallized hydrate.

[5] Nichols and Snow: Phil. Mag. [5], **32**, 423 (1891). The comparatively rare phenomena of "surface color" are, of course, excluded from consideration.

In a more finely powdered pigment there will be obviously more surface per unit of mass, and the first of these "interior faces" will be on the average nearer the external surface of the layer; that is, the layer of colored material through which the internally reflected ray must pass, is less in the finely powdered material. It must therefore happen that the selective absorption which takes place in this ray will be relatively weaker or in common phrase, the "color" imparted to the ray will be less marked. In the terms of the curve expressing the relation between intensity and wave length in the reflected light, what happens may be expressed as a flattening of the curve or a decreasing of the accentuation of the maximum (or maxima) to which (with the physiological amendments below noted) the visual color is due. In the simplest case, therefore, the effect of pulverization of pigment should be simply to weaken the color or dilute it with white.[1] The natural deduction is that the more finely a substance is powdered the more nearly white it will become, though a limit will finally be reached beyond which the individual particles become comparable in size to the wave length of light and hence change their optical behavior. Many colored substances are actually white or nearly white when finely pulverized,[2] and nearly all colored bodies show a tendency in this direction.

Lead chromates, however, show a more complex behavior. The original reddish orange of crocoite changes on grinding to a clear yellow with no apparent trace of red, and this clear yellow is characteristic of all finely divided samples of $PbCrO_4$. None of them become white. This seems to

[1] It is perhaps unnecessary to point out that visual white and spectral white are not necessarily the same thing. To the retina, red and yellow are the opposites of green and blue respectively, and each pair of opposites is algebraically summed. A light is visually white when the red is of equal physiologic intensity to the green and the yellow equal to the blue This is not necessarily the same as the (ideal) spectral white in which the light is of equal intensity in all wave lengths.

[2] For instance, colored quartzes and fluorspars, garnet, obsidian, cobalt glass, manganous salts, nickel-ammonium salts, etc., etc.

indicate not only a weakening of the total color as described, but an actual change in color, a shifting of the (visual) maximum from the red or orange into the yellow. The explanation of this effect requires a reference to the spectrum of the light reflected by lead chromate. This has been investigated by Nichols,[1] who obtained the curve given in Fig. 1, where the abscissae represent wave lengths and the ordinates intensities in terms of the spectrally uniform ideal white.

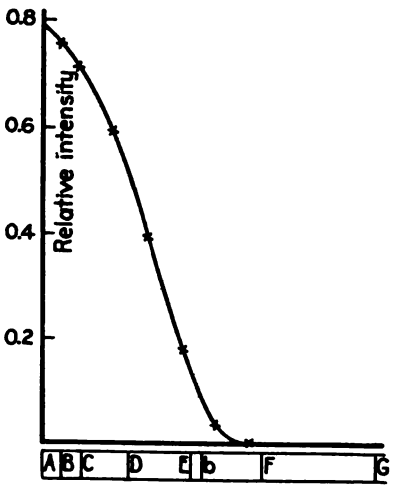

Fig. 1

Spectrum of light reflected from lead chromate. Ordinates indicate relative intensities in terms of ideal white. After Nichols.

The curve may be legitimately considered as the representation of the light which is allowed to pass by a thin plate of lead chromate. It is the reverse of the ordinary absorption curve which indicates the parts of the spectrum in which the light is retained by the body under examination. Considering the curve in this way it is apparent that lead chromate absorbs practically all the blue and violet, most of the green and a considerable fraction of the yellow, but allows the red (and probably the infra-red) to pass in much greater degree and in increasing proportion with increasing wave length. In other

[1] Am. Jour. Sci. [3], 28, 345 (1884).

words, there is an absorption area or "band" extending out of the ultra-violet into the visible spectrum, across the violet and blue, and shading off in the green and yellow. When the transmitted light is observed by the eye the green component is physiologically neutralized and overcome by the much larger quantity of red which has been permitted to pass, and the apparent color is a shade of yellow or orange with a greater or less tinge of red.

How will these relations be affected by change in the thickness of the plate of pigment? Optical absorption bands in most bodies deepen on increase of thickness of the absorbing medium, and also spread out laterally, extending themselves into the regions of the spectrum contiguous on either side. This spreading is not always symmetrical but is most frequently approximately so; and in the case under discussion, since definite data are lacking, it may be assumed that the general rule is followed. If, therefore, the thickness of the chromate plate be increased, the area of absorption, represented by the lower portion at the right-hand end of the curve, will extend itself toward the left, successively extinguishing the green, yellow, and red until in the extreme case the plate will have become totally opaque to visible radiations. It is evident, therefore, that with increase of thickness of the absorbing plate the light transmitted by lead chromate should become (as indeed it does) more and more deeply red. It is perhaps worth noting that the extension of the absorption band into the green produces, in the apparent color, a disproportionate strengthening of the red, for the removal of the green releases and makes physiologically active that fraction of the red which was previously employed in neutralizing in the retina the excitation due to the presence of the green.

If, on the other hand, the thickness of the absorbing plate be decreased, the absorption area will retreat toward the violet, the high part of the curve (indicating more complete transmission) will move toward the right, and, successively the yellow, the green, and the blue will be allowed to pass. In the limiting case, which is probably not actually realizable,

the absorption area would move altogether beyond the visible spectrum, making the plate visually transparent. In intermediate cases the retreat of the absorption area and the progressive transmission of the green will progressively weaken the red by physiological neutralization, and thus make the yellow more and more prominent in the apparent color of the transmitted light. At the same time the yellow is further strengthened by its own progressively more complete transmission. It is therefore evident that with decrease in thickness of the plate of pigment the reddish tones of the apparent color will disappear and will be replaced by clear yellows. When the plates are very thin, the yellow itself is in part physiologically neutralized by the blue which begins to be transmitted, and the apparent color changes, never back to red (for there is always more green transmitted than blue), but to a paler and paler yellow and ultimately (in the limiting case) to white.

All this concerns the light *transmitted* through thin plates, but the application to the case in which light is *reflected* from a non-homogeneous layer of pigment is easy and obvious. It has already been pointed out that the colored fraction of the light reflected from (nearly) all bodies is light which has passed through a greater or less thickness of the material and suffered selective absorption. However, in the light reflected from a mass of powdered pigment there does come into play another factor—the reflection of white light from external faces of the crystals, as already discussed. The only effect of this is to dilute the color with white and render color differences less pronounced and less easily perceptible.

Practically then we should expect just what occurs. The larger crystals should be redder and the smaller more purely yellow. In very finely powdered samples the color should be much diluted with white and therefore very "clear." It is even conceivable that pulverization might be pushed to a point where the body would become white, though whether this is practically realizable is problematical. Of the facts as stated there is no question, but the explanations advanced can have

no certain validity in the absence of direct experimental evidence.

If the above discussion is correct, it is possible to draw the practical deduction that the occasional cases of turning, which are apparently not due to increase of basicity, may possibly be caused by change in the coarseness of the precipitate. With increase of crystal size, the precipitate will take on a darker, redder, and less brilliant color.[1] The color is practically the same as that caused by a slight basicity, and is exactly that observed when the pigment "turns." The differences in crystal size may be caused by variations in the concentration or temperature of the precipitating solutions,[2] or may be due to secondary changes which take place when the precipitate is allowed to stand in contact with the mother liquor. It is well known that all crystalline precipitates do tend to increase in coarseness when allowed to stand in this way.[3]

The discussion of the color changes, which correspond to changes in size of crystal in the case of the basic chromates, is impossible in the absence of reliable determinations of the spectra of these bodies. Their behavior is probably quite analogous to that of the neutral chromate. It is known that the yellow tinge shown by finely ground chrome red is really present in the color at all times, for it makes its appearance when this pigment is combined with others which wholly or partially neutralize the red component. On account of this yellow tinge chrome red has been highly recommended for the production of flesh tints in painting.[4]

Color and Temperature

Lead chromate is one of the many so-called "metachro-

[1] In technical phrase, a "dirty color."

[2] It will be shown in the experimental part of this paper that such variations do have an influence on the crystal size.

[3] Rothmund: Löslichkeit und Löslichkeits beeinflussung, p. 109 (1907). Cf. also Chesneau-Principes théoretiques des methodes d'analyse minerale, pp. 16–25 (1906).

[4] Fuss: loc cit.

matic"[1] substances which change their color on heating. In this regard it is quite regular and follows the vast majority of other substances in that the maximum intensity moves toward the red with rise of temperature.[2] When the neutral chromate is heated the color ranges through the orange to a very deep red,[3] and in natural crocoite almost to black.[4] Chrome red and melanochoite also darken in a similar manner when heated.[5] The original colors are in all cases recovered on cooling; in fact, Houston and Thompson have shown that the general tendency of the color intensity to move towards the red with heating exists also in the reverse direction. Cooled to —30° or —40° the neutral chromate becomes a yellowish green.[6]

These colors are, of course, due directly to the temperature possessed by the body and have nothing to do with the permanent color differences seen in samples of lead chromate precipitated at different temperatures. These latter doubtless correspond to chemical or morphological modifications

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[1] Ackroyd: Chem. News, **34**, 75 (1876).

[2] Schönbein: Pogg. Ann. [2], **15**, 263 (1838). Houston and Thompson: Chem. News, **24**, 177, 188 (1871). Ackroyd, and Nichols and Snow: loci citati. In connection with these observations of the effect of heating on color there is an interesting fact which, though quite different in cause, may serve as an illustration of the discussion in the last section. White metachromatic bodies almost invariably become yellow on heating. If metachromatism consist, as is probable, of a general movement of intensity toward the red, the yellowing of white bodies means simply that the blue has been suppressed and the yellow is therefore no longer physiologically neutralized. The case is the same as with finely ground lead chromate, the green is able to neutralize the red, and only the yellow remains visible. On further heating, the green might disappear and the body would pass through the orange into the red, as does the chromate with increasing crystal size. In practice, the color changes on heating are soon complicated and obscured by light *emitted* by the body, as was found by Nichols and Snow to be the case with zinc oxide.

[3] Marchand: Jour. prakt. Chem., **19**, 65 (1840). Berzelius: Traité de Chimie, Vol. IV, p. 109 (1847). Dana: System of Mineralogy, 6th Ed., p. 914 (1892). Houston and Thompson: loc. cit.

[4] Dana: loc. cit.

[5] Houston and Thompson: loc. cit. Gmelin-Kraut: Handbuch anorg. Chem., Vol. III, p. 279 (1887).

[6] Houston and Thompson: loc. cit., p. 188.

of the chromate crystals and are probably to be ascribed either to the effect of the temperature of precipitation on the size of the crystals or to the tendency of hot precipitation to cause an increase in the basicity of the precipitate.

III. EXPERIMENTS ON THE CHEMICAL PRECIPITATION OF LEAD CHROMATE

A molecular solution of $Pb(NO_3)_2$ was prepared by dissolving 331 grams of the crystalline salt in a liter of distilled water; 500 cc of this solution were then diluted to one liter, 500 cc of the resultant solution again diluted to one liter, and this process repeated until a series of 15 solutions was obtained, each member of which had a concentration equal to one-half that of the preceding member. A similar series of solutions of K_2CrO_4 was then prepared, starting with a molecular solution (194.3 grams per liter) as before. Thus the solutions of corresponding number in the two series were chemically equivalent, the most concentrated being molecular, and the most dilute M/16384.

Preliminary tests showed that the manner of mixing the solutions in making a precipitation had much influence on the character of the precipitate produced—probably because of concentration changes occasioned by incomplete mixing. This trouble was partially avoided by the following method of precipitation: 50 cc of one of the solutions were placed in a 200 cc beaker and stirred vigorously by means of an electrically operated stirrer, while 50 cc of the equivalent solution of the other series were added in a slow stream. The mixture was then stirred for exactly five minutes, then taken out and the character of the precipitate examined. The same 50 cc pipette was used in all cases to measure the solutions.

Accidental and irregular variations in the precipitate are not by any means entirely avoided by this method of precipitation, but the results are much more uniform than by the ordinary method of pouring the solutions together. For precipitations at a temperature above that of the room,

the beaker in which the precipitation was made was immersed in a dish containing water at the desired temperature. It seemed on trial that it made no constant difference in the character of the resulting precipitate whether the chromate solution was poured into the lead solution, or vice-versa; consequently, the former order was adopted in all cases. The precipitates were examined by the eye for color and state of aggregation (coarseness), comparison being made in each case between a whole series of precipitates made at different concentrations. Sedimentation tests were made by diluting the precipitates with their mother liquor until all contained the same quantity of precipitate in unit volume, and observing the rate at which these mixtures settled when placed in test-tubes. All of these methods of comparison gave more or less erratic results, which was probably due in part to faults in the method and in part to accidental variations in conditions. By far the most reliable indications were given by the microscope, and the best method of observation was found to be as follows: A small drop of the precipitate and mother liquor was placed on a slide, covered with a cover glass, and the latter rubbed around a little to break up the aggregations of the crystals. The most uniform parts of the slide were then observed with a magnification of 1100 diameters and the average size of the crystals determined by means of a micrometer eye-piece. The method of making color comparisons is described later.

General Character of the Precipitates

The precipitates are subject to very great irregularities. Two precipitates prepared as nearly as possible in the same manner will differ markedly in color, crystal size, tendency to flocculate, etc., etc. These variations are undoubtedly due to uncontrolled differences in the manner of precipitation, although what these differences may be it is impossible to say from the knowledge at present available. It must be understood, of course, that the variations in the precipitates are only relative. All the precipitates are yellow; all

of them are composed of very fine particles. In fact, all have the characteristic properties of precipitated $PbCrO_4$. The differences appear only on close examination.

It is believed that all the precipitates are crystalline, although in a few cases it was impossible to detect individual crystals. In most cases the precipitate appears under the microscope as a mass of interwoven needle-like prisms which are very easily broken up into short prismatic fragments. The crystal angles could not be determined. The smaller fragments almost invariably showed strong Brownian movements when suspended in water. Apparently in all cases lead chromate is first formed in colloidal solution and then precipitated, the rate of precipitation increasing with the concentration, *i. e.*, the amount of electrolyte (KNO_3) in the solution. In the very dilute solutions lead chromate remains in colloidal solution for several days. The rapidity of precipitation is much hastened by heating.

Effect of Temperature on Precipitation

Series of precipitations from solutions of various concentrations were made at about 20° and at 90° C. From solutions of the same concentration the precipitates thrown down at the higher temperatures were uniformly darker in color and almost uniformly composed of larger crystals. The exceptions to this latter rule were found only in the higher concentrations, where the crystals were so small that accurate measurements became practically impossible. The precipitates thrown down at 90° were much more uniform in character and apparently much less subject to the influence of accidental variations in conditions than were those made at 20°.

Effect of Concentration of Precipitating Solutions

Since accidental variations appeared to have less influence at high than at low temperatures, the influence of concentration was studied on precipitates prepared at 90°. A series of 15 of these precipitates was prepared from the solutions described on page 128. The precipitates from solutions of a concentration of M/512 (No. 10) and less were so small

in amount that comparisons of color were impossible. The precipitates from solutions 1 to 9 inclusive (concentrations M to M/256) were examined as to color by comparing each precipitate with every other precipitate in the series and noting in each case which was darker. When in any comparison a certain precipitate was called darker than another one, it was counted as a "score" for the darker precipitate. If no color difference could be detected between the two precipitates no score was counted for either. Thus when the comparisons were all finished and the scores belonging to each precipitate added up, the darkest precipitate of the series had the highest total of scores (since it had been most often marked as darker), and hence in a rough way the total of the scores marked against each precipitate indicated its "darkness" (or deepness, or redness) of color.[1] The indications were made more accurate by giving each score more or less weight as the precipitate obtaining it was much or little darker than the one with which it was being compared. Thus if precipitate A was much darker than precipitate B it received a score of 5; if only slightly darker, of 1, etc.

A set of such scores obtained on precipitates from solutions 1 to 9 is given in Table I. A higher total of scores indicates (at least roughly) a darker precipitate.

TABLE I

Effect of concentration of precipitating solutions on color of precipitate. Precipitations made at 90°

Number	Concentration in gram molecules per liter	Color score (Higher score means darker)
1	1	0
2	1/2	6
3	1/4	9
4	1/8	26
5	1/16	14
6	1/32	19
7	1/64	9
8	1/128	4
9	1/256	0

[1] This method is one which has been devised and used by the experimental psychologists.

These data are shown graphically in Fig. 2. On account of their great range it is impossible to represent the concentrations to scale. In the curve the numbers of the precipitates are simply set down in the *order* of concentration on the axis of abscissas, while the corresponding total scores are plotted as ordinates. Thus the point corresponding to a given precipitate stands at a height above the base line (axis of abscissas) roughly proportional to the comparative darkness of color of that particular precipitate.

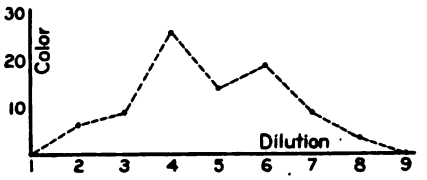

Fig. 2

Relation of the concentration of the precipitating solutions to the color of the precipitate. Precipitations at 90°.

It is apparent that the curve shows a tendency to rise in the middle, which means that these precipitates are darker in color than the rest. There seems therefore to be a maximum of darkness or deepness of color in the precipitates from concentrations of 1/8 to 1/32 g mols per liter. This conclusion is borne out in a general way by another series of precipitates, the results of which are given in Table II and shown in Fig. 3. This series was precipitated at 20° instead of 90°, and only every other concentration was taken.

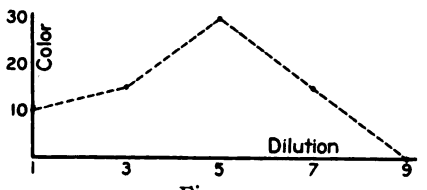

Fig. 3

Relation of the concentration of the precipitating solutions to the color of the precipitate. Precipitations at 20°.

TABLE II

Effect of concentration of precipitating solutions on color of precipitate. Precipitations made at 20°

Number	Concentration in gram molecules per liter	Color score (Higher score means darker)
1	1	10
3	1/4	15
5	1/16	30
7	1/64	50
9	1/256	0

The effect of the concentration of the precipitating solutions on the size of the precipitated crystals was followed by measuring under the microscope a series of precipitates produced as already described. In each case there was noted: (1) the length of the longest crystals in the preparation; (2) the length of the shortest crystals (excluding broken crystals where possible); (3) the length which seemed to be approached most nearly by the largest number of crystals.[1] These three lengths are designated as the "maximum," "minimum" and

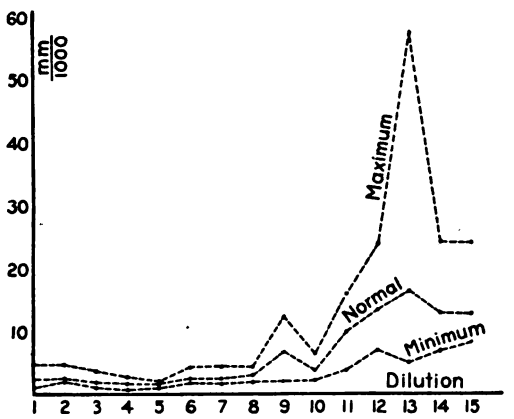

Fig. 4

Relation of the concentration of the precipitating solutions to the size of crystals in the precipitate.

[1] Not necessarily the *average* length.

"normal," respectively. It is believed that the normal length is at least a moderately exact index of the prevailing crystal size of the precipitate. The measurements are given in Table III and shown graphically in Fig. 4. In this curve as in others the concentrations are not plotted to scale.

TABLE III

Effect of concentration of precipitating solutions on the crystal size of the precipitate

Number	Concentration in gram molecules per liter	Length of crystal in thousandths of a millimeter		
		Maximum	Minimum	Normal
1	1	4.8	0.8	2.1
2	1/2	4.8	1.6	2.4
3	1/4	3.2	0.5	1.8
4	1/8	2.4	0.4	1.2
5	1/16	1.6	0.4	1.2
6	1/32	4.0	1.2	1.9
7	1/64	4.0	1.2	1.9
8	1/128	4.0	1.6	2.4
9	1/256	12.8	1.6	6.4
10	1/512	6.4	1.6	3.2
11	1/1024	16.0	3.2	9.6
12	1/2048	24.0	6.4	12.8
13	1/4096	57.6	4.8	16.0
14	1/8192	24.0	6.4	12.8
15	1/16384	24.0	8.0	12.8

These measurements, of course, apply only to the *length* of the crystals, that being the dimension susceptible to most accurate measurement. Rough measurements of width and of area covered in the microscopic field show general agreement with those made on length.

In spite of considerable irregularities in the results, there is, as might be expected, an unmistakable tendency for the size of the crystal to rise with decrease of concentration, all three curves showing the same general tendency. This increase of the crystal size with decrease of concentration is in a general way a matter of common knowledge, and

goes hand in hand with the well-known tendency, which was also observed in these experiments, for dilute solutions to require a much longer time for complete precipitation than do concentrated ones.

Effect of Glue in the Solution

A series of precipitates was prepared as above except that to each solution there had been added sufficient white glue (in solution) to make a concentration of 10 grams per liter. These precipitates differed from the former ones mainly in the slowness with which they formed. Precipitates were formed immediately only in the most concentrated solutions, and in the solutions more dilute than 1/36 molecular no solid precipitate was formed at all. The solutions simply turned yellow and opalescent, remaining thus for several months. The retarding action of the glue is less marked the higher the temperature of precipitation.

The precipitates from solutions containing glue are always composed of finer particles than those from ordinary solutions of corresponding concentration. In general the color is lighter.

Summary

The experimental results may be summed up as follows:

1. The largest crystals are obtained in hot and dilute solutions.

2. The precipitates from the most concentrated and the most dilute solutions are lighter in color than those from the intermediate solutions.

3. Glue retards precipitation and causes the formation of smaller crystals.

It will be noted that the results on the effect of the concentration of the precipitating solutions on color and on crystal size, are not, when taken together, in accord with the theories outlined in the second part of this paper. It has been found that the size of the precipitated crystals increases continuously with decrease in concentration. If then the color of the precipitate were directly and exclusively dependent on

its coarseness, the color should show a continuous increase in darkness in the same direction. This it does not do. The curve of darkness of color shows a maximum at the moderate concentrations. This is probably due to the existence of a number of causes which are independently affecting the color of the precipitate. Indeed, that there are at least two such causes at work is proven by the very fact that the color curve shows an inversion. A curve corresponding to only one physical law shows no inversions. The two most probable causes of color change are varying basicity and varying size of crystal, and it may be that these two in combination are competent to produce the observed effects. More than this cannot be said until the conditions which control variations of basicity have been more fully and more accurately investigated.

The practical application of these results to the art of pigment manufacture depends upon the fact that a chrome yellow of small crystals possesses a clearer color and, other things equal, a greater covering power, than one of large crystals. Hence the best conditions for the manufacture of chrome yellow, other things being equal, should be cold and concentrated solutions mixed with rapid stirring under conditions which would most successfully prevent the formation of basic salt.[1] What these last conditions are can only be settled by further investigation. It is an interesting question whether the presence of glue in the solutions would have any disadvantageous effect. The matter of oil absorption

[1] It is possible that the recommendations of concentrated solutions and the prevention of the formation of basic salt are mutually incompatible. It may be that the use of concentrated solutions would in itself cause the precipitate to become partially basic. It is claimed by many pigment experts that this is the case. If so, it would be necessary for practical purposes to reach a compromise between, on the one hand, the tendency of dilute solutions to produce coarse precipitates; and on the other, the tendency of concentrated solutions to induce basicity. To this question, as to others, a complete answer cannot be given without further investigation of the production of the basic salts. The data of Table I would seem to indicate that very concentrated solutions are not, however, incompatible with low basicity.

is another important question which must some day be taken up.

The results so far obtained must, of course, be considered as tentative and as subject to revision. The methods of testing the character of the precipitate leave much to be desired, and the variables affecting the character are not yet controlled adequately. Some means should be devised whereby all the precipitations could be made under exactly the same conditions of mixing of the two solutions, of stirring, etc. If we had such means, work on the character of the precipitates formed from other lead salts or from solid lead compounds, or in the presence of colloids, organic liquids, solid particles, etc., etc., ought to be both interesting and valuable.

While the net results of this investigation have not been large, the paper will have served its purpose if it calls attention to the interesting possibilities involved in a systematic study of the conditions affecting the production and properties of pigments.

The investigation was suggested by Professor Bancroft and carried on under his direction. I am glad to have opportunity of acknowledging my great indebtedness to him not alone in this matter but in many others.

Cornell University

A SIMPLE METHOD FOR VAPOR-DENSITY DETERMINATIONS

BY PHILIP BLACKMAN

PART VI

The Dissociation of Phosphorus Pentachloride

The method employed was that described by the author,[1] the heating medium being paraffin wax contained in an oblong sheet-iron trough, but no glass jacket round the bulb (as a protection against possible bursting) was employed. The pentachloride began to disappear, *i. e.*, to volatilize, at about 160°–170°, the vaporization being complete at about 180°; some of the substance could be seen previously existing in a liquid condition. The total time occupied in the readings for l and t_2° was about 3 hours. The densities (d) as calculated by the author are, at corresponding temperatures, greater than those determined by Dumas, and this is no doubt due to the fact that under the considerable internal pressures of the bulb the pentachloride dissociated to a smaller extent than it would have done under normal atmospheric pressures. The formula used for the calculation of the pressures (in atmospheres) is

$$\pi = pL(273 + t_2)/760l(273 + t_1).$$

The readings for l at 180°, 175°, and 170° were taken while the thermostat was cooling down.

[1] Jour. Phys. Chem., 12, 661 (1908).

(d_1 = 52.06 = the vapor-density of $PCl_3 + Cl_2$; d_2 = 104.12 = the vapor-density of PCl_5); w = 0.1465 gram; V = 34.6 cc; L = 202 mm; L_c = 212 mm; t_1 = 18° C; p = 760 mm

t_2°	l mm	d (author's)	π (atmospheres)	w_1 % ($PCl_3 + Cl_2$)	100 − w_1 % (PCl_5)	d (Dumas')
170	130	83.80	2.36	24.24	75.76	
175	129	82.16	2.41	26.74	73.26	
180	128	80.55	2.45	29.25	70.75	72.5
185	127	78.98	2.50	31.82	68.18	(at 182°)
190	124	74.48	2.59	39.78	60.22	
195	123	73.05	2.64	42.53	57.47	
200	121	70.58	2.71	48.14	51.86	69.2
205	120	68.95	2.76	50.42	49.58	
210	119	67.64	2.81	53.94	46.06	
215	118	66.36	2.87	56.90	43.10	
220	117	65.11	2.92	59.93	40.07	
225	116	63.88	2.98	63.00	37.00	
230	115	62.67	3.03	66.14	33.86	
235	114	61.49	3.09	69.33	30.67	
240	113	60.33	3.15	72.57	27.43	
245	112	59.20	3.21	75.86	24.14	
250	111	58.19	3.27	79.22	20.78	57.0

PART VII

The Dissociation of Chloral Hydrate

The bulb was heated in a thermostat (containing paraffin wax), but no protective glass jacket (as a safeguard against possible bursting) was used. The hydrate melted at about 96°, and the liquid had a considerable vapor-pressure, as was evident by a very marked decrease in the length of L_c. At any temperature the vapor-density varies directly as the pressure (until the substance is completely decomposed into the vapors of chloral and water); hence the extent of the dissociation diminishes (at corresponding temperatures) with increase of pressure. The pressures (in atmospheres) were calculated by means of the formula

$$\pi = pL(273 + t_2)/760\,l(273 + t_1).$$

Forcrand[1] calculated that at 100°, under ordinary atmospheric pressure, 4 to 5 percent of the vapor of chloral hydrate is undissociated. The complete dissociation of the substance takes place in such a very short range of temperature that the results cannot be used with the slightest hope of obtaining anything like a reliable result in the calculation of the heat of formation of chloral hydrate from chloral and water in the gaseous state, and the estimations thus offer no information towards the controversy on the subject that took place between Berthelot[2] and Würtz.[3]

[d_1 = 41.34 = vapor-density of chloral and water;
d_2 = 82.67 = vapor-density of chloral hydrate.]

EXPERIMENT I

w = 0.1903 gram; p = 763 mm; V = 25.5 cc; t_1 = 18° C; L = 212 mm; L_c = 232 mm

t_2°	l mm	d vapor-density	w_1 % (H_2O + $CCl_3.COH$)	$100 - w_1$ % $CCl_3.CH(OH)_2$	π atmospheres
105	106	81.35	1.62	98.38	2.61
106	104	78.56	5.22	94.78	2.66
107	101	74.55	10.89	89.11	2.75
108	99	71.98	14.85	85.15	2.78
109	97	69.48	18.99	81.01	2.88
110	96	68.35	20.97	79.03	2.92
111	94	65.87	25.47	74.53	2.99
112	92	63.55	30.09	69.91	3.06
113	90	61.15	35.19	64.81	3.13
114	88	59.09	39.89	60.11	3.21
115	86	56.96	45.14	54.86	3.30
116	85	55.92	47.85	52.15	3.34
117	84	54.52	51.65	48.35	3.39
118	83	53.86	53.46	46.54	3.45
119	82	52.86	56.38	43.62	3.47
120	81	52.85	56.41	43.59	3.55

[1] Comptes rendus, **133**, 474 (1901).
[2] Ibid., **85**, 13 (1877); **92**, 826 (1881).
[3] Ibid., **89**, 1099; **90**, 24, 337, 491, 572 (1880).

EXPERIMENT II

$w = 0.3646$ gram; $p = 761$ mm; $V = 26.6$ cc; $t_1 = 17°$ C; $L = 176$ mm; $L_c = 190$ mm

$t_2°$	l (mm)	d	w_1	$100 - w_1$	π
130	58	76.97	7.40	92.60	4.21
135	50	62.57	32.12	67.88	4.95
140	45	54.37	52.03	47.97	5.57
145	42	49.72	66.28	33.72	6.04
150	39	45.25	82.70	17.30	6.58
155	37	42.37	95.14	4.86	7.02

EXPERIMENT III

$w = 0.2254$ gram; $p = 761$ mm; $V = 33.4$ cc; $t_1 = 17°$ C; $L = 163$ mm; $L_c = 176$ mm

$t_2°$	l (mm)	d	w_1	$100 - w_1$	π
103	86	80.56	2.61	97.39	2.43
105	84	78.77	4.96	95.04	2.53
108	79	70.26	17.68	82.32	2.71
110	76	67.09	23.22	76.78	2.83
113	70	56.96	45.09	54.91	3.10
115	67	53.03	55.93	44.07	3.25
120	64	49.29	67.68	32.32	3.45
125	59	43.50	90.03	9.97	3.79
130	58	42.41	94.94	5.06	3.90
135	57	41.32	100.00	0.00	4.02
140	57	41.32	100.00	0.00	4.14
145	57	41.32	100.00	0.00	4.18
150	57	41.32	100.00	0.00	4.22

PART VIII

The Dissociation (Decomposition by Heat) of Aldehyde-Ammonia

The apparatus used and method of procedure were the same as those detailed by the author in the previous papers.[1] The extent of the dissociation increases with increase of temperature, and, at corresponding temperatures, the greater the total internal pressure the smaller is the

[1] Jour. Phys. Chem., 12, 661 (1908).

degree of the dissociation; similarly at like internal pressures the percentage dissociation is greater the higher the temperature.

Experiment I

$w = 0.0236$ gram; $L = 163$ mm; $L_c = 177$ mm; $p = 745$ mm; $V = 28$ cc; $t_1 = 17°$ C

t_2 °C	l mm	d density	w_1 %($CH_3.CHO + NH_3$)	$100 - w_1$ % $CH_3.CH(OH)NH_2$	π (atmospheres)
103	109	17.75	72.02	23.98	1.90
104	107	16.91	80.39	11.61	1.94
105	105	16.14	89.06	10.94	1.98
106	103	15.40	98.10	1.90	2.03
107	103	15.40			
108	103	15.40			
109	103	15.40			
110	103	15.40			

Experiment II

$w = 0.0449$ gram; $L = 185$ mm; $L_c = 202$ mm; $p = 745$ mm; $V = 23.5$ cc; $t_1 = 17°$ C

t_2°	l	d	w_1	$100 - w_1$	π
103	101	25.23	19.86	80.14	2.33
104	98	23.77	28.37	71.63	2.40
105	94	21.96	38.99	61.01	2.51

Experiment III

$w = 0.0255$ gram; $L = 157$ mm; $L_c = 170$ mm; $V = 30$ cc; $p = 767$ mm; $t_1 = 16.5°$ C

t_2°	l	d	w_1	$100 - w_1$	π
103	106	17.87	70.70	29.30	1.94
104	104	16.67	83.09	16.91	1.98
105	102	16.19	88.53	11.47	2.03
106	101	15.80	93.18	6.82	2.05
107	100	15.42	97.97	2.03	2.08

EXPERIMENT IV

$w = 0.0402$ gram; $L = 188$ mm; $L_c = 201$ mm; $V = 26.1$ cc; $p = 767$ mm; $t_1 = 16.5°$ C

$t_2°$	l	d	w_1	$100 - w_1$	π
103	110	23.34	30.80	69.20	2.24
104	108	22.42	36.11	63.89	2.29
105	105	21.12	44.49	55.51	2.36
106	104	20.71	47.44	52.56	2.39
107	102	19.89	53.34	46.66	2.44
108	101	19.50	56.49	43.51	2.47
109	100	19.12	59.65	40.35	2.50

[d_1 = vapor-density of $CH_3.CHO + NH_3$; d_2 = vapor-density of undissociated $CH_3.CH(OH).NH_2$].

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TABLES OF MOLECULAR CONDUCTIVITIES[1]

BY PHILIP BLACKMAN

The author showed in the *Philosophical Magazine*, 11, 418 (1906), that the equations

$$\begin{aligned} &\mu v_{M_1.OH} - \mu v_{M_2.OH} \\ &= \mu v_{M_1X} - \mu v_{M_2X} \\ &= \mu v_{M_1X_1} - \mu v_{M_2X_1} \\ &= \mu v_{M_1X_2} - \mu v_{M_2X_2} \\ &= \ldots\ldots\ldots\ldots \\ &= \text{constant,} \end{aligned}$$

(in which $\mu v_{M_1.OH}$, $\mu v_{M_2.OH}$, μv_{M_1X}, μv_{M_2X}, etc., represent the molecular conductivities, all measured at the same concentration v and at the same temperature, of the bases $M_1.OH$ and $M_2.OH$, and of the salts M_1X, M_2X, etc., respectively) can be used to calculate the molecular conductivities of salts and bases, whether soluble or insoluble, or stable or unstable in aqueous solution. The following tables give the results of a large number of molecular conductivities calculated by the aid of the above equations. Table I gives molecular conductivities at 18°, and Table II those at 25°. If the values be calculated by means of the equations[2]

$$\mu v_{M_1.OH} = \mu v_{M_1} + \mu v_{OH}, \text{ etc., and } \mu v_{M_1X} = \mu v_{M_1} + \mu v_X, \text{ etc.}$$

[1] In continuation of the papers in Proc. Chem. Soc., 21, 237 (1905); Chem. News, 93, 284; 94, 164, 176 (1906); 95, 133 (1907); Phil. Mag., 11, 416; 12, 150, 532 (1906); 14, 215 (1907).

[2] Phil. Mag., 12, 151 (1906); Chem. News, 94, 176 (1906), using the quantities there given. The results will be found in remarkably close agreement with the numbers here given.

TABLE I

$v =$	10000	5000	2000	1000	500	200	100	50	33·3	20	10	5	3·33	2	1
$LiBr$	101	100	99	98	97	96	93	91	—	89	86	82	—	77	—
LiI	100	99	98	97	96	95	93	91	—	88	86	—	—	78	76
LiF	89	81	78	77	76	75	73	71	—	67	63	—	—	55	48
$LiClO_3$	89	89	88	86	86	85	84	82	—	78	76	—	—	67	63
$LiC_2H_3O_2$	69	68	68	67	66	65	64	60	—	58	54	51	48	44	35
$\frac{1}{2}Li_2CO_3$	—	—	—	—	97	90	84	78	75	71	64	57	53	48	43
$\frac{1}{2}K_2SiO_3$	—	—	—	165	163	160	157	153	150	145	137	126	119	109	96
$\frac{1}{3}K_2HPO_4$	—	—	—	79	78	—	75	—	71	69	64	—	—	55	51
$NaBr$	111	109	108	107	106	105	103	101	—	97	93	89	—	84	—
NaI	110	109	107	106	105	104	102	100	—	96	93	—	—	84	82
$NaSCN$	99	99	98	97	96	95	94	91	—	87	83	—	—	75	71
$NaClO_3$	98	97	96	95	94	93	91	88	—	82	78	72	—	64	—
$\frac{1}{2}Na_2C_2O_4$	104	103	102	101	99	95	92	87	—	80	73	68	—	—	53
LiC_2O_4	94	94	93	92	90	86	83	78	—	71	65	59	—	—	46
$TlBr$	133	132	132	132	129	127	125	124	—	118	113	110	—	107	—
TlI	131	130	130	129	128	126	124	122	—	118	112	—	—	108	100
$TlClO_3$	120	119	119	118	117	115	112	109	—	104	98	94	—	87	—
$\frac{1}{2}TlCO_3$	—	—	—	(134)	130	124	116	110	107	102	92	87	(83)	80	67
$\frac{1}{2}TlC_2O_4$	126	126	125	123	122	119	114	109	—	102	93	89	—	—	·70
$\frac{1}{3}TlH_2PO_4$	—	—	—	33	32	—	30	—	29	28	25	—	—	23	17
$TlIO_3$	99	99	98	97	96	94	92	89	—	80	72	—	—	—	—
$TlC_2H_3O_2$	102	102	101	100	98	96	95	93	—	89	82	(79)	(76)	74	60
$\frac{1}{2}Tl_2SO_4$	132	131	131	130	—	121	117	111	—	103	93	(88)	—	81	68
$AgCl$	119	118	117	116	115	113	112	109	—	104	102	98	—	92	88
$AgBr$	120	119	119	118	117	115	113	110	—	107	103	99	—	94	—

TABLE I—(*Continued*)

$v =$	10000	5000	2000	1000	500	200	100	50	33·3	20	10	5	3·33	2	1
AgI	119	119	118	118	117	114	113	111	—	107	103	—	—	95	92
AgF	100	99	98	97	96	95	93	92	—	87	83	—	—	72	65
$AgClO_3$	107	107	106	105	104	103	102	98	—	94	88	83	—	74	—
$AgIO_3$	87	86	86	85	84	82	80	78	—	73	69	63	—	—	—
$\frac{1}{2}Ag_2CO_3$	—	—	—	(122)	117	111	114	98	—	90	83	76	72	68	60
$AgC_2H_3O_2$	89	88	87	87	86	85	83	80	79	77	73	68	65	60	52
$\frac{1}{2}Ag_2SO_4$	120	119	117	116	—	109	105	100	—	91	84	77	—	67	61
$\frac{1}{2}Ag_2C_2O_4$	114	114	113	112	110	106	102	97	—	90	84	77	—	—	63
CsBr	136	135	134	133	132	130	128	125	—	121	117	113	—	107	—
CsI	135	134	133	131	130	128	126	124	—	120	116	—	—	108	105
CsF	114	113	112	111	110	109	107	105	—	101	97	—	—	86	78
Cs.CSN	124	123	122	121	120	119	117	115	—	110	107	—	—	98	94
$Cs.ClO_3$	122	121	120	119	118	117	115	112	—	107	102	97	—	87	—
$Cs.IO_3$	101	100	99	98	97	96	94	92	—	87	82	76	—	—	—
$CsNO_3$	129	128	127	126	125	124	121	118	—	113	108	102	—	91	82
$Cs.C_2H_3O_2$	104	103	102	101	100	99	97	95	94	91	87	82	78	74	65
$\frac{1}{2}Cs_2.SO_4$	134	133	131	130	—	124	119	113	—	105	98	91	—	81	73
RbBr	136	135	134	133	132	130	128	125	—	121	117	113	—	107	—
RbI	135	134	133	131	130	128	126	124	—	120	116	—	—	108	105
RbF	114	113	112	111	110	109	107	105	—	101	97	—	—	86	78
$RbNO_3$	129	128	127	126	125	124	121	118	—	113	108	102	—	91	82
$Rb.C_2H_3O_2$	104	103	102	101	100	99	97	95	94	91	87	82	78	74	65
$\frac{1}{2}Rb_2.SO_4$	134	133	131	130	—	124	119	113	—	105	98	91	—	81	73
Rb.SCN	124	123	122	121	120	119	117	115	—	110	107	—	—	98	94
$Rb.ClO_3$	122	121	120	119	118	117	115	112	—	107	102	97	—	87	—

TABLE I—(*Continued*)

$v =$	10000	5000	2000	1000	500	200	100	50	33·3	20	10	5	3·33	2	1
$Rb.IO_3$	101	100	99	98	97	96	94	92	—	87	82	76	—	—	—
$\frac{1}{2}Rb_2CO_3$	—	—	—	(137)	132	125	118	112	109	104	97	90	85	80	72
$\frac{1}{2}Rb_2C_2O_4$	129	128	127	126	124	122	116	111	—	104	97	91	—	—	75
$\frac{1}{3}RbH_2PO_4$	—	—	—	35	34	33	32	—	31	30	29	—	—	25	23
$\frac{1}{2}Cs_2CO_3$	—	—	—	(137)	132	125	118	112	109	104	97	90	85	80	72
$\frac{1}{2}Cs_2C_2O_4$	129	128	127	126	124	122	116	111	—	104	97	91	—	—	75
$\frac{1}{3}CsH_2PO_4$	—	—	—	35	34	33	32	—	31	30	29	—	—	25	23
$\frac{1}{2}ZnBr_2$	110	109	108	105	101	95	92	87	—	83	78	72	—	62	—
$\frac{1}{2}ZnI_2$	109	108	107	106	100	96	91	86	—	81	77	—	—	63	61
$\frac{1}{2}ZnF_2$	90	89	88	84	82	71	70	66	—	60	56	—	—	44	34
$\frac{1}{2}Zn(SCN)_2$	99	98	97	96	90	83	81	77	—	73	70	—	—	58	50
$\frac{1}{2}Zn(ClO_3)_2$	98	97	96	93	89	81	79	74	—	69	65	58	—	48	—
$\frac{1}{2}Zn(IO_3)_2$	77	76	74	72	68	62	60	54	—	49	44	39	—	—	—
$\frac{1}{2}Zn(NO_3)_2$	105	104	102	100	96	90	86	80	—	75	70	63	—	51	38
$\frac{1}{2}Zn(C_2H_3O_2)_2$	79	78	77	74	70	65	62	57	55	53	49	43	40	34	22
$\frac{1}{2}ZnCO_3$	—	—	—	(109)	101	91	83	74	70	66	59	52	46	40	29
$\frac{1}{2}ZnC_2O_4$	104	103	101	98	93	86	81	73	—	66	60	53	—	—	32
$\frac{1}{2}BaBr_2$	121	120	119	118	116	112	106	104	—	92	86	82	—	77	—
$\frac{1}{2}BaI_2$	120	119	118	117	117	111	105	103	—	91	85	—	—	78	75
$\frac{1}{2}BaF_2$	100	99	98	97	93	90	86	82	—	78	70	—	—	55	48
$\frac{1}{2}BaSO_4$	120	119	118	111	—	104	98	90	—	80	73	68	—	50	44
$\frac{1}{2}BaCO_3$	—	—	—	(121)	112	105	97	89	84	79	72	62	58	50	43
$\frac{1}{2}Ba(ClO_3)_2$	108	107	106	104	100	97	93	88	—	82	77	68	—	57	—
$\frac{1}{2}Ba(IO_3)_2$	87	86	85	84	80	77	73	69	—	62	58	51	—	—	—
$\frac{1}{2}BaC_2O_4$	115	114	113	110	105	101	95	88	—	79	73	60	—	—	46

TABLE I—(*Continued*)

$v =$	10000	5000	2000	1000	500	200	100	50	33·3	20	10	5	33·3	2	1
$\frac{1}{2}MgBr_2$	111	110	109	107	106	96	94	91	—	82	79	75	—	68	—
$\frac{1}{2}MgI_2$	109	108	107	102	101	100	93	91	—	82	78	—	—	67	65
$\frac{1}{2}MgF_2$	90	89	88	87	81	80	76	74	—	67	60	—	—	45	38
$\frac{1}{2}Mg(ClO_3)_2$	98	97	96	95	94	88	82	79	—	74	64	59	—	47	—
$\frac{1}{2}Mg(IO_3)_2$	77	76	75	74	69	67	61	59	—	54	45	40	—	—	—
$\frac{1}{2}Mg(NO_3)_2$	74	103	102	101	100	94	89	85	—	80	69	62	—	51	42
$\frac{1}{2}Mg(C_2H_3O_2)_2$	79	78	76	74	73	69	64	61	59	58	49	44	39	34	25
$\frac{1}{2}MgCO_3$	—	—	—	112	107	99	85	79	76	66	59	50	45	40	33
$\frac{1}{2}MgC_2O_4$	104	103	102	100	98	90	83	78	—	71	60	53	—	—	36
$\frac{1}{2}CuCl_2$	110	109	108	107	105	101	98	94	—	87	83	78	—	69	61
$\frac{1}{2}CuBr_2$	110	109	108	107	105	95	93	89	—	82	78	74	—	66	—
$\frac{1}{2}CuI_2$	109	108	107	103	101	98	92	89	—	81	77	—	—	65	63
$\frac{1}{2}CuF_2$	90	89	88	85	81	75	73	70	—	63	58	—	—	44	36
$\frac{1}{2}Cu(ClO_3)_2$	98	97	96	95	94	85	80	76	—	71	68	59	—	47	—
$\frac{1}{2}Cu(IO_3)_2$	77	76	75	73	68	65	60	56	—	52	44	39	—	—	—
$\frac{1}{2}Cu(NO_3)_2$	104	103	102	101	98	92	87	82	—	78	69	62	—	51	40
$\frac{1}{2}Cu(C_2H_3O_2)_2$	79	78	76	74	71	67	63	59	57	55	49	44	39	34	23
$\frac{1}{2}CuCO_3$	—	—	—	111	103	95	84	76	73	66	59	51	45	40	31
$\frac{1}{2}CuC_2O_4$	104	103	101	99	95	88	82	77	—	69	60	53	—	—	34
$\frac{1}{2}PbCl_2$	125	124	122	120	117	112	107	102	—	93	81	73	—	52	46
$\frac{1}{2}PbBr_2$	126	125	123	121	118	113	109	104	—	95	83	75	—	—	—
PbI_2	125	124	123	122	117	112	108	104	—	95	83	—	—	56	51
$\frac{1}{2}PbF_2$	106	105	104	102	99	94	90	84	—	71	64	—	—	36	30
$\frac{1}{2}Pb(ClO_3)_2$	114	113	112	110	106	102	96	90	—	87	64	59	—	40	—
$\frac{1}{2}Pb(IO_3)_2$	93	92	91	89	86	81	76	70	—	67	50	36	—	—	—

TABLE I—(*Continued*)

$v =$	10000	5000	2000	1000	500	200	100	50	33.3	20	10	5	33.3	2	1
$\frac{1}{2}Pb(C_2H_3O_2)_2$	95	94	93	91	88	84	79	73	67	61	53	44	40	25	15
$\frac{1}{2}PbSO_4$	126	125	123	120	—	108	101	92	—	75	64	53	—	34	26
$\frac{1}{2}PbCO_3$	—	—	—	126	119	109	108	91	83	74	61	52	45	25	17
$\frac{1}{2}PbC_2O_4$	120	119	118	115	110	105	98	90	—	71	63	54	—	—	28
$\frac{1}{2}(NH_4)_2CO_3$	—	—	—	132	127	122	116	109	106	101	93	86	82	77	70
$\frac{1}{2}(NH_4)_2C_2O_4$	124	124	124	122	120	117	113	108	—	101	94	88	—	—	73
$NH_4.C_2H_3O_2$	99	99	99	98	97	96	94	91	90	87	83	78	75	71	62
$NH_4.SCN$	119	119	119	119	118	116	114	111	—	108	103	—	—	95	91
$NH_4.F$	109	109	109	109	108	106	104	102	—	98	93	—	—	82	75
$\frac{1}{2}(NH_4)_2SO_4$	130	129	129	127	—	120	116	110	—	102	94	87	—	77	71
NH_4Br	130	130	130	129	128	126	124	122	—	118	113	119	—	104	—
NH_4I	129	128	128	128	127	125	123	121	—	117	113	—	—	105	103
NH_4F	109	109	109	109	108	106	104	102	—	98	93	—	—	81	75
$\frac{1}{2}CaBr_2$	117	116	114	113	112	108	105	102	—	96	91	87	—	82	—
$\frac{1}{2}CaI_2$	116	115	113	112	111	107	104	101	—	95	90	—	—	88	80
$\frac{1}{2}CaF_2$	97	95	94	93	92	88	85	82	—	77	71	—	—	60	53
$\frac{1}{2}Ca(ClO_3)_2$	106	105	103	102	100	96	93	89	—	84	76	71	—	62	—
$\frac{1}{2}Ca(IO_3)_2$	84	83	82	81	79	75	72	69	—	62	57	51	—	—	—
$\frac{1}{2}CaCO_3$	—	—	—	118	112	104	96	89	84	78	71	64	60	55	48
$\frac{1}{2}CaC_2O_4$	111	110	109	107	104	99	93	88	—	78	72	66	—	—	50
$\frac{1}{2}SrBr_2$	119	118	117	115	113	110	107	102	—	96	91	86	—	81	—
$\frac{1}{2}SrI_2$	118	117	116	114	112	109	106	101	—	95	90	85	—	82	74
$\frac{1}{2}SrF_2$	98	97	96	95	93	90	87	82	—	76	71	—	—	59	47
$\frac{1}{2}Sr(ClO_3)_2$	107	106	105	103	101	98	95	89	—	82	76	70	—	61	—
$\frac{1}{2}Sr(IO_3)_2$	85	84	83	82	80	77	74	69	—	62	57	51	—	—	—

TABLE I—(*Continued*)

$v =$	10000	5000	2000	1000	500	200	100	50	33.3	20	10	5	33.3	2	1
$\frac{1}{2}SrSO_4$	118	117	116	113	—	104	99	80	—	80	72	64	—	55	43
$\frac{1}{2}SrCO_3$	—	—	—	(119)	113	106	99	89	85	79	71	63	59	54	42
$\frac{1}{2}SrC_2O_4$	112	111	110	108	105	101	96	88	—	79	72	65	—	—	44
Li.OH	—	—	—	204	203	200	198	195	192	189	183	176	173	167	153
Tl.OH	—	—	—	236	235	232	230	227	224	219	215	208	205	200	186
Ag.OH	—	—	—	224	223	220	218	215	212	207	203	196	193	188	174
Cs.OH	—	—	—	238	236	233	231	228	225	222	215	208	205	199	186
Rb.OH	—	—	—	237	235	232	231	228	225	222	215	208	205	200	186
$NH_4.OH$[1]	—	—	—	234	233	230	228	225	222	219	211	205	201	196	183
$\frac{1}{2}Zn(OH)_2$	—	—	—	214	213	210	205	203	98	95	—	—	—	—	—
$\frac{1}{2}Ba(OH)_2$	—	—	—	224	223	219	214	212	208	214	197	189	186	180	167
$\frac{1}{2}Mg(OH)_2$	—	—	—	214	213	210	207	204	201	197	191	183	180	174	161
$\frac{1}{2}Cu(OH)_2$	—	—	—	214	213	210	198	196	192	189	178	170	160	149	140
$\frac{1}{2}Pb(OH)_2$	—	—	—	230	228	224	221	217	212	204	198	181	173	161	154
$\frac{1}{2}Ca(OH)_2$	—	—	—	230	228	226	223	218	213	206	200	191	183	177	162
$\frac{1}{2}Sr(OH)_2$	—	—	—	230	228	226	223	217	212	205	199	190	182	175	160

[1] Compare the values given in the Chemical News, 95, 133 (1907).

TABLE II

$v =$	32	64	128	256	512	1024
KH_4IO_6	115	119	121	124	126	127
$\frac{1}{2}K_2H_3IO_6$	100	110	119	129	133	134
$\frac{1}{3}K_3H_2IO_6$	137	150	157	160	161	161
$\frac{1}{2}K_5IO_6$	173	186	192	194	193	193
KH_2PO_4	97	100	103	105	107	109
$\frac{1}{2}K_2HPO_4$	107	113	118	121	124	124
$\frac{1}{3}K_3PO_4$	126	136	144	147	147	147
$\frac{1}{4}K_4P_2O_7$	102	113	124	133	138	141
$\frac{1}{2}K_2WO_4$	118	124	133	134	136	139
$\frac{1}{2}K_2MoO_4$	123	129	133	138	140	144
$\frac{1}{2}K_2SeO_4$	123	128	133	138	140	144
$KAsO_2$	100	104	110	113	116	119
$\frac{1}{2}K_2HAsO_4$	106	113	117	121	124	126
$\frac{1}{3}K_3AsO_3$	191	194	194	194	194	194
$\frac{1}{2}K_3AsO_4$	123	134	144	150	150	150
$\frac{1}{2}K_2S_2O_5$	94	100	103	104	104	104
$\frac{1}{2}K_2B_4O_7$	94	99	102	104	107	110
$\frac{1}{2}K_2B_2O_4$	95	100	103	106	109	112
$\frac{1}{2}K_2CO_3$	93	97	119	130	137	143
$NaBrO_3$	92	96	99	100	101	103
$\frac{1}{2}Na_2SO_4$	102	109	115	118	123	125
$\frac{1}{2}Na_2CrO_4$	108	114	119	121	125	128
$\frac{1}{2}Na_2Cr_2O_7$	100	102	104	105	105	106
$\frac{1}{2}Na_2S_2O_8$	125	113	120	123	127	130
$\frac{1}{2}Na_2CO_3$	72	85	97	108	115	120
$NH_4.Br$	137	140	145	147	149	149
NH_4I	137	140	144	146	148	149
NH_4F	114	118	120	122	124	125
$NH_4.NO_3$	128	132	136	138	141	141
$NH_4.NO_2$	148	151	155	158	161	166
$\frac{1}{2}(NH_4)_2SO_4$	124	131	137	141	145	148
$\frac{1}{2}(NH_4)_2SO_3$	119	126	131	135	138	143
$NH_4.HSO_3$	109	113	118	121	125	129
$\frac{1}{2}(NH_4)_2CO_3$	93	107	119	130	137	143
$RbBr$	139	143	147	150	152	152
RbI	139	143	147	149	151	152
RbF	117	120	123	125	127	128
$RbNO_2$	150	154	157	161	164	169
$\frac{1}{2}Rb_2SO_4$	126	134	142	144	148	151
$\frac{1}{2}Rb_2CrO_4$	131	139	144	148	151	152
$Rb.HSO_3$	110	116	120	124	130	131
$\frac{1}{2}Rb_2CO_3$	95	109	122	132	139	144
$\frac{1}{2}Rb_2SO_3$	122	128	133	138	142	146

TABLE II—(*Continued*)

$v =$	32	64	128	256	512	1024
$RbClO_3$	125	129	133	135	137	138
$RbClO_4$	133	138	142	146	148	149
$RbMnO_4$	124	128	131	133	133	134
CsBr	139	143	147	150	152	152
CsI	140	144	148	149	152	152
CsF	118	121	124	126	128	129
$Cs.NO_2$	151	155	158	162	165	170
$\frac{1}{2}Cs_2SO_4$	127	135	143	145	149	152
$\frac{1}{2}Cs_2CrO_4$	132	139	145	149	152	153
$Cs.HSO_3$	111	117	121	125	131	132
$\frac{1}{2}Cs_2CO_3$	96	110	123	133	140	144
$\frac{1}{2}Cs_2SO_3$	123	129	134	139	143	147
$CsClO_3$	126	130	134	136	138	139
$CsClO_4$	134	139	143	147	149	150
$CsMnO_4$	125	129	132	134	134	135
LiBr	104	108	112	115	117	117
LiF	82	85	88	90	92	93
$LiNO_2$	115	118	120	125	128	134
$\frac{1}{2}Li_2SO_4$	91	98	105	109	113	116
$\frac{1}{2}Li_2CrO_4$	97	103	109	113	116	118
$\frac{1}{2}Li_2Cr_2O_7$	89	91	93	93	94	97
$Li.HSO_3$	76	81	85	90	93	97
$\frac{1}{2}Li_2SO_3$	86	93	98	103	107	111
TlBr	137	141	145	148	150	151
TlI	137	141	144	147	149	150
$TlMnO_4$	122	125	128	130	131	132
$TlNO_2$	147	151	155	159	162	166
$\frac{1}{2}Tl_2CrO_4$	129	136	141	145	148	150
$\frac{1}{2}Tl_2Cr_2O_7$	122	124	125	126	127	129
$\frac{1}{2}Tl_2SO_3$	119	126	131	136	139	143
$\frac{1}{2}Mg(ClO_3)_2$	98	102	105	108	110	110
$\frac{1}{2}Mg(ClO_4)_2$	106	110	115	118	120	121
$\frac{1}{2}Mg(BrO_3)_2$	89	93	96	98	100	101
$\frac{1}{2}MgI_2$	112	115	120	122	123	125
$\frac{1}{2}MgF_2$	90	93	96	98	100	101
$\frac{1}{2}Mg(NO_3)_2$	103	107	110	114	116	117
$\frac{1}{2}MgCr_2O_7$	97	100	101	101	102	104
$\frac{1}{2}MgSO_3$	94	101	106	110	114	118
$\frac{1}{2}NiBr_2$	109	114	120	124	127	128
$\frac{1}{2}NiI_2$	109	103	119	122	125	126
$\frac{1}{2}NiF_2$	86	92	96	100	102	103
$\frac{1}{2}Ni(NO_2)_2$	119	123	129	135	138	143
$\frac{1}{2}CoBr_2$	109	114	120	123	126	127

TABLE II—(*Continued*)

$v =$	32	64	128	256	512	1024
$\frac{1}{2}CoI_2$	108	102	118	121	124	125
$\frac{1}{2}CoF_2$	85	91	95	99	101	102
$\frac{1}{2}Co(NO_2)_2$	118	122	128	134	137	142
K.OH	232	240	247	251	251	251
Na.OH	211	219	226	230	230	230
Rb.OH	232	242	249	253	254	254
Cs.OH	231	242	249	254	255	255
Li.OH	197	206	215	218	219	219
$\frac{1}{2}Mg(OH)_2$	204	214	222	227	228	228
$\frac{1}{2}Ni(OH)_2$	203	214	221	226	228	228
$\frac{1}{2}Co(OH)_2$	202	213	220	225	226	227

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NOTE ON THERMODYNAMIC EQUILIBRIUM AND STABILITY

BY J. E. TREVOR.

The conditions that must be satisfied, to ensure that a given r-phase state of an n-component body shall be a stable thermodynamic state, are due to Gibbs. Gibbs obtains these conditions of equilibrium and stability by applying the general criterion of thermodynamic equilibrium and stability to variations of state that leave the volume and entropy of the body unchanged. It may not be generally recognized that this restriction is unnecessary. The criterion in question can be readily applied to the general variation of the state of the body. The present note presents the simplest possible illustration of this modification of Gibbs's procedure, by applying it to the case of a one-component body.

Consider any given r-phase state of an n-component body supporting the uniform pressure p at the absolute temperature θ. If, in every possible variation of this thermodynamic state, the concurrent variations of the energy E, the volume V, and the entropy S, of the body satisfy the relation

$$\delta E + p\delta V - \theta\delta S = \theta\Sigma, \tag{1}$$

the state is stable; otherwise it is not. In this relation, the quantity $\theta\Sigma$ is zero when the initial state and the varied state are contained in a continuous assemblage of states all of which are stable under the pressure p at the temperature θ. For all other variations, $\theta\Sigma$ is positive. The general criterion (1) of equilibrium and stability is an expression of the principle that a body, in any spontaneously occurring change of its thermodynamic state, passes to the stable state determined by the imposed conditions, and thereby loses as much as possible of its ability to develop work.

In any quiescent r-phase state of a one-component body,

the energy of the body is the sum of the energies of the r phases,

$$E = E_1 + E_2 + \ldots + E_r;$$

and each of the phase-energies E_i can be expressed as a continuous one-valued function of the volume, entropy, and mass of the phase,

$$E_i(V_i, S_i, M_i). \qquad (i = 1,2 \ldots r)$$

Within the region of stable states of the phase, each of the phase-variables V_i, S_i, M_i can be independently varied. It is assumed that this is the case at every realizable stable state of the phase. The first derivatives of the function E_i are the pressure p_i, the absolute temperature θ_i, and the potential h_i of the phase. The volume V and the entropy S of the body, expressed as functions of the phase-variables, are

$$\begin{aligned} V &= V_1 + V_2 + \ldots + V_r \\ S &= S_1 + S_2 + \ldots + S_r; \end{aligned}$$

and the variables are subject to the relation

$$M = M_1 + M_2 + \ldots + M_r,$$

where the mass M of the body is a constant.

By means of the equations of the preceding paragraph, the criterion (1) is expressed *analytically* by the equation

$$\begin{aligned} &- p_1\delta V_1 + \theta_1\delta S_1 + h_1\delta M_1 + \delta^2 E_1 + \ldots \\ &- \ldots \\ &- p_r\delta V_r + \theta_r\delta S_r + h_r\delta M_r + \delta^2 E_r + \ldots \\ &+ p\delta V_1 + \ldots \quad + p\delta V_r \\ &- \theta\delta S_1 - \ldots \quad - \theta\delta S_r = \theta\Sigma; \end{aligned}$$

which is subject to the condition

$$\delta M_1 = -\delta M_2 - \ldots - \delta M_r.$$

Eliminating the dependent variation δM_1, and collecting terms, we obtain

$$\begin{aligned} &- (p_1 - p)\delta V_1 - (p_2 - p)\delta V_2 - \ldots - (p_r - p)\delta V_r \\ &+ (\theta_1 - \theta)\delta S_1 + (\theta_2 - \theta)\delta S_2 + \ldots + (\theta_r - \theta)\delta S_r \\ &\qquad + (h_2 - h_1)\delta M_2 + \ldots + (h_r - h_1)\delta M_r \\ &\qquad + \delta^2(E_1 + E_2 + \ldots + E_r) + \ldots \quad = \theta\Sigma. \end{aligned}$$

For the contrary variation, from the state

$$V_i, \qquad S_i, \qquad M_i,$$

to the state

$$V_i - \delta V_i, \qquad S_i - \delta S_i, \qquad M_i - \delta M_i,$$

the signs of the terms of odd orders in the above equation will be reversed. Accordingly, for variations small enough to cause the first member of the equation to have the sign of the sum of terms of the first order, this sum must be zero; else it would be positive for one variation and negative for the contrary one.

Further, since only independent variations appear as factors in the terms of the first order, each of the variations but any one can be made to vanish. It follows that the conditions of equilibrium and of stability, involved in the criterion of equilibrium and stability, are:

$$\begin{aligned} p = p_1 = p_2 = \ldots &= p_r \\ \theta = \theta_1 = \theta_2 = \ldots &= \theta_r \\ h_1 = h_2 = \ldots &= h_r, \end{aligned}$$

which are the conditions of equilibrium; and

$$\delta^2(E_1 + E_2 + \ldots + E_r) = 0,$$

a formulation of the conditions of stability. When the values of the phase-variables satisfy these conditions, the r-phase state of the body is a stable state; otherwise it is not.

THE ACTION OF OXALIC ACID UPON FERRIC HYDROXIDE[1]

BY F. K. CAMERON AND W. O. ROBINSON

There is very little mention of ferric oxalates in the literature. G. Lemoine[2] found that oxalic acid and ferric chloride react very slowly with one another at ordinary temperatures but rapidly at temperatures above 100° in a sealed tube. He does not, however, describe the solid phase he obtained, since the object of his research was the rate of reduction of ferric chloride. Rosenheim[3] found that freshly precipitated ferric hydroxide dissolved in oxalic acid to form a deep yellow, syrupy solution of the composition $Fe_2O_3 . 3C_2O_3xH_2O$.

In connection with studies of the action of various acids upon ferric hydroxide, the system Fe_2O_3, C_2O_3 and H_2O has been studied in part at 25° C. Oxalic acid solutions of various concentrations were put in contact with ferric hydroxide and at the end of three months the solutions and remaining solid phases were analyzed. The iron was determined in the usual gravimetric manner. The oxalic acid was determined by titration with permanganate. In the analysis it was noticed that approximately one-tenth of the total amount of permanganate used for each determination was immediately reduced in the cold. It was necessary to heat the liquid to accomplish the rest of the reduction. From these facts it appears that about one-tenth of the oxalic acid had disappeared in reducing the iron to the ferrous condition.

The analytical results are given in Table I, and show, when plotted, that the solubility of the ferric oxide is directly proportional to the concentration of oxalic acid, and that no definite basic ferric oxalate is formed from solution at 25° C. At all concentrations, the solution contains more iron than is

[1] Published by permission of the Secretary of Agriculture.

[2] Comptes rendus, 116, 981–2 (1893).

[3] Zeit. anorg. Chem., 11, 175–222 (1896).

equivalent to the oxalic acid present, but as is usual with solutions of ferric salts, all these solutions had an acid reaction by the ordinary tests.

TABLE I

Showing the solubility of ferric hydroxid in aqueous solutions of oxalic acid and the composition of the solid phases with adhering solution.

Solution			Solid + adhering solution	
Sp. gr.	Percent Fe_2O_3	Percent C_2O_3	Percent Fe_2O_3	Percent C_2O_3
1.007	0.48	0.61	32.71	3.01
1.015	0.95	1.23	—	—
1.031	1.86	2.45	32.93	4.02
1.040	2.33	3.10	—	—
1.050	2.98	3.85	30.56	5.31
1.064	3.62	5.17	34.25	5.98

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NEW BOOKS

Bacteria in Relation to Country Life. *By Jacob G. Lipman. 13 × 19 cm; pp. xviii + 486. New York: The Macmillan Company, 1908. Price: $1.50 net.*—The subject is divided into eight parts: structure and growth of bacteria; bacteria in air and water; bacteria and sewage; bacteria in relation to soil fertility; bacteria in barnyard manure; bacteria in milk and related products; bacteria in relation to preservation of food; bacteria and fermentation. The book is an interesting one and can be opened almost anywhere with profit. The following quotations will illustrate this.

"Intimately connected with the life processes of bacteria is the ability of some species to produce pigments. The coloring matters produced by different species include golden yellow, orange, red, blue, pink, violet, green, brown, and black substances. Blue or red milk, and even bluish or yellow pus in wounds may be produced by bacteria."

"The ability to produce phosphorescence is a property held by certain species of bacteria in common with some members of the animal kingdom. These bacteria, designated as *photobacteria*, are, so far as is known, all inhabitants of the sea. The phosphorescence of sea-water, a phenomenon much commented upon, is due largely, though not entirely, to bacteria. It is these organisms, also, that produce phospho escence in decaying fish and meat."

"*Bacteria and respiration.*—The number of bacteria in the air over the ocean, over high mountains, in polar regions, or in countries of scant rainfall, is relatively very small. Conditions there prevent both the addition of large numbers to the atmosphere, as well as the survival of the bacteria already there. On the contrary, the air of city streets and of human dwellings is particularly rich in microörganisms owing to conditions favoring both the addition of large numbers to the atmosphere and their survival there.

"These facts are of very considerable moment from the standpoint of hygiene and sanitation. We know that, notwithstanding the large number of bacteria in the atmosphere, the air expired from the human lungs is practically germ-free. This means that the microörganisms are retained in the nose, mouth, and throat, and that many of them are carried with the dust particles into the lungs. Enormous numbers of bacteria are thus retained, and it is obvious that, everything being equal, the danger from infection is greatest when the number of bacteria in the air is greatest. Persons leading an indoor existence, and those living in large cities, inhale more bacteria and are more exposed to infection than people living in the country.

"It does not follow, at the same time, that the danger of contracting a disease, say tuberculosis, is greater in the summer than it is in the winter, simply because there are more germs abroad. After all, most of the bacteria in the air are harmless, and it is very likely that the actual number of the germs of tuberculosis and pneumonia in the winter air is greater than that in the summer air."

"*Self-purification of rivers.*—The activities of the water and sewage bacteria rapidly exhaust the store of readily decomposable organic material. The less readily available residues do not furnish the large quantities of food required

by vast numbers of bacteria, and the less resistant species are rapidly eliminated in the struggle for existence. The gradual disappearance from the water of the organic substances, as well as of the bacteria introduced with the sewage into flowing streams is designated as self-purification."

"*Filters for domestic purposes.*—There are various types of small filters for domestic use. It is well-known that most bacteria are held back by filters made of unglazed porcelain. Some species exist, however that are so small as to pass the minute pores of these filters. For practical purposes, nevertheless, unglazed porcelain may be regarded as bacteria-tight, and water which passes through as sterile. This fact has led to the use of such filters for the purification of water used in the home. With many people no doubt seems to exist as to their permanent efficiency. Unfortunately, however, there are conditions under which such filters are not bacteria-tight. To be sure, the organisms cannot pass through them directly, yet it has been demonstrated quite forcibly that they can *grow through them.*

"Any of these filters, kept moist for some time, and accumulating organic matter on the inside and in their pores, will, finally, become pervious to the bacteria in them. Typhoid germs, as well as other microörganisms, may thus find their way into the supposedly pure water and cause disease. To render the porcelain filters absolutely safe it is necessary to burn them out from time to time, so that all of the organic matter contained in them may be destroyed. Unglazed porcelain filters that can be thus renovated with but slight danger of breaking are now being made.

"Other filters for domestic use, made of charcoal or blocks of sandstone, possess the same defects noted in the porcelain filters, and should not be depended upon for the purification of drinking-water for any considerable length of time. They should be thoroughly cleaned and boiled at least once a week if their efficiency is to be assured."

"Freezing temperatures destroy a large proportion of the bacteria in the water. They cannot, however, be depended upon to destroy all of the bacteria, and thus render the water sterile. This has been repeatedly demonstrated by various investigators. Careful studies have been made in this connection with the typhoid bacillus, the cholera germ, the anthrax bacillus, and a number of non-pathogenic organisms. It has been proved that ice may become a source of infection and disease. The process of freezing is often, in itself, insufficient for the complete destruction of all the bacteria present in the water.

"Under certain conditions, the longevity of the typhoid germs and other bacteria may be considerably reduced. This is particularly so when the process of freezing is not continuous, but consists of alternate periods of freezing and thawing.

"Such intermittent freezing may lead to the destruction of the typhoid, cholera, and other organisms within a few days; whereas, spore-producing species, like the anthrax bacillus, are not thus destroyed, owing to the great resistance of the spores. Everything considered, then, ice made from polluted water must be regarded with suspicion. Artificial ice, on the other hand, when made from distilled water, is almost free from bacteria, and may be used safely in the household. Artificial ice made from river-, well-, or spring-water con-

tains a variable number of bacteria, depending on the purity of the water employed.

"Bacteriological examinations of thick cakes of natural ice have shown that, as the freezing proceeds from the top downward, the number of bacteria included in the ice diminishes. The greatest proportion of bacteria has been found to occur in the snow-ice, although on the whole, there seems to be no uniform distribution of the bacteria in any one layer. Their number may vary from less than one hundred to several thousand per cubic centimeter. As the ice melts, the number of bacteria in the ice-water begins to increase, attaining at times, very considerable proportions. One instance is reported in which a piece of ice was melted and immediately examined. The number of organisms per cubic centimeter, was 1020, whereas, eleven days later the ice-water was found to contain 220,000 bacteria.

"The partial destruction of the bacteria by freezing, and their subsequent multiplication in the ice-water, may have a direct bearing on the typhoid question, since it has been observed that not all of the bacteria are affected to the same extent by freezing. It is quite possible that the disease germs may survive in much greater proportion than the harmless bacteria, and may subsequently multiply as the ice melts. Typhoid germs do not appear to suffer from the competition of other bacteria at lower temperatures so much as they suffer from it at higher temperatures. Savage states that "at the temperature of the ice-chest, the typhoid germ may grow in the by-products of other germs, which, at higher temperatures, are quickly fatal to it."

"In September, 1881, a patent for 'The Automatic and Odorless Scavenger' was granted to Mouras in France. The American patent granted to Mouras is dated November 28, 1882. The patents were preceded by twenty years of practical experience, which left no doubt as to the remarkable efficiency of the process in destroying organic matter. The construction of the 'Scavenger' was very simple. It consisted of an air-tight, hermetically sealed tank, supplied with a feed-pipe to receive evacuations, kitchen wastes, and the like, and an outlet in the upper part of the tank for the discharge of the sewage. Both of the pipes dipped under the surface of the liquid in the tank which was completely filled with water before being placed in service. When anything was discharged into the feed-pipe, an equal volume of liquid was expelled from the tank. The liquid expelled contained disintegrated and largely decomposed material. It is evident that the organic matter introduced into the tank was destroyed by anaërobic bacteria. So rapid was the process of decomposition that the excreta was dissolved in eighteen days, while resistant substance, like paper, disappeared in a comparatively short time, with the formation of products largely gaseous in character. The Mouras 'Automatic Scavenger' may thus be regarded as the predecessor of the modern 'septic tank,' an important feature of all efficient sewage-purification plants."

"Profitable sewage-farming is, however, exceptional. By far the greatest number of sewage-farms do not yield a profit. Especially is this the case when the initial outlay for land and equipment is included in the charges. The failure of sewage-farms to return a profit is not difficult to understand if we remember that the land near large cities is very costly, that large areas are required for sewage treatment, and that the range of crops grown is frequently limited.

Moreover, the proportion of manurial constituents in sewage is, after all, so slight as to make the application of very large quantities necessary in order that an adequate supply of plant-food may be furnished to the soil. At a generous estimate, English sewage may be allowed a value of three or four cents per ton, while American sewage cannot be valued at much more than a cent per ton on the basis of its manurial ingredients. 'As Professor Anderson suggested long ago,' says Storer, 'it would be about as reasonable to expect the farmers to manure their land with the smoke of cities as with sewage; for, as every one knows, enormous quantities of ammonia must be lost in the aggregate from cities where domestic fires are fed with soft coal. But precisely as it is with the smoke, so it is with sewage; that is to say, the fluid is so very dilute that it cannot be put to use."

"*The crops grown on sewage farms.*—These must be capable of transpiring large quantities of water, and must otherwise be adapted to the soil conditions. Italian rye grass has been grown extensively on the sewage-farms in England and Scotland. It grows very rapidly, crowds out weeds, and yields several heavy cuttings in one season. It requires reseeding every three years, although usually it is succeeded at the end of that time by other crops, like mangolds or cabbages. On some of the irrigated meadows the rye grass has been replaced by a mixture of native grasses which likewise produce heavy yields of dry matter. Alfalfa has also been grown successfully on sewage-irrigated lands near Paris and in our western states. Like the Italian rye grass, it transpires enormous quantities of water. On the whole, however, leguminous crops are not adapted for sewage-farms."

"There exists unquestionably an important relation between the crop on the soil and the numbers and kinds of bacteria within it. For one thing, the leafy crops that shade the soil create conditions as to moisture, temperature and light that are different from those created by cereal crops. The differences do not, by any means, stop there. The crops take plant-food and moisture from the soil and give back to it some of their substance, something that passes out of the roots and into the soil. Our knowledge of the amount and nature of the substances thus given up to the soil by the plants is meager. It is not known as yet to what extent these secretions influence the numbers and kinds of bacteria in the soil. There is reason to believe, however, that a decided influence is thus exerted by the growing crops. These affect the growth of soil bacteria in still another way.

"It is a well-known fact that different crops do not take out of the store of available constituents in the soil the same amounts and proportions of plant-food. For this reason, they affect the composition of the soil to an unequal extent and unequally change the numbers and character of the soil bacteria. The effects of different systems of cropping are clearly distinguishable both in the size and quality of the harvests and in the endurance of soil fertility. The pernicious effects of the continuous growing of cereals were noted generations ago, and led gradually to the introduction of rotation systems. It seems that the evil effects of continuous grain-growing are due in part to the one-sided and wasteful changes in the soil-humus caused by bacteria. On the other hand, a succession of different crops, including members of the legume family, creates conditions favoring an economical transformation of the soil-humus. It will

thus be seen that there is a direct relation between the crops on the soil and the bacteria in the soil.

"The number of soil bacteria varies likewise with the methods of tillage. All of the mechanical operations, such as plowing, harrowing, disking, hoeing, and rolling, which affect the evaporation from the soil, the penetration of air, or the supply of moisture from the subsoil by capillary action, affect the rate of increase of the soil bacteria. The numbers of bacteria in the soil are readily affected by the application of manures and fertilizers as well as by the turning under of green-manures. When any of these manurial substances are introduced into the soil, there are changes produced in its content of soluble salts, and, likewise, modifications in its moisture and aëration conditions. An additional factor is introduced in the case of barnyard manure, since the latter is a material rich in bacteria. An application of several tons of manure per acre introduces into the soil many millions of bacteria, and not only adds thus to the numbers already present there, but also influences the rate of subsequent increase."

"*Quality of humus as affecting number of bacteria.*—The influence of the quality of humus on the soil bacteria is also important. The so-called *mild humus*, or *mull*, of arable soils, or of woodland, is different in its composition from the *raw humus* of heaths, meadows, and swamps. It influences in an entirely different way the numbers and character of the bacteria. The differences observed are due largely to the origin and mode of formation of the two classes of humus substances. The mild humus is formed under conditions admitting the free access of air and through the activities largely of aërobic organisms. It is either neutral or alkaline in reaction. The raw humus is formed through the process of putrefaction rather than that of decay. It is acid in reaction, and is not a suitable medium for the development of most bacteria. It has been shown that peat lands contain a relatively slight number of bacteria before they are reclaimed and placed under cultivation. When drained and limed, the number of bacteria soon increases from a few thousands to many millions per gram of soil."

"*Importance of nitrification.*—The vast practical significance of nitrification processes is apparent from the fact that most of the nitrogen used by crops is taken up in the nitrate form. While there is much evidence at hand to show that many plants are capable of utilizing ammonia as readily as nitrate nitrogen, yet, because of the very rapid conversion of ammonia into nitrate, the latter is almost the exclusive source of nitrogen. The rapidity with which ammonia salts are changed in the soil to nitrates is attested by the experience at Rothamsted in England. It was the practice there to apply the nitrogen on certain plots in the form of ammonium sulphate in the fall. It was soon noticed, however, that, notwithstanding the lateness of the season, the ammonia was rapidly converted into nitrate as shown by the increased contents of the latter in the drainage-water from those plots. In fact, the application of the ammonia salts was practically equivalent to the application of nitrate, and, in order to guard against the loss of nitrogen, the fall applications of ammonia salts were discontinued."

"It has already been stated that the application of ammonia salts in the fall is wasteful because of its ready conversion into nitrate, even in the late fall.

In fact, nitrification seems to go on until the soil is almost frozen. When a crop is occupying the land, the nitrate as it is formed is taken up by the plants and but little allowed to escape into the drains. When the land is kept bare, the nitrates formed are washed into the deeper layers of the soil and may be carried off by the drainage. It is for this reason partly that the continuous growing of wheat is a wasteful procedure. The land is kept bare at a time of the year when the nitrification processes in the soil are most active, resulting in the loss of very considerable quantities of nitrates. Investigations have shown that in the continuous growing of wheat there may be four to six pounds of nitrogen lost from the soil to every pound removed in the crop."

"*Soil-inoculation in the United States.*—The history of soil-inoculation efforts in the United States is, in many respects, unique. As in Germany, the first attempts at inoculation involved the application of legume-earth as inoculating material. Crops like clovers, cow-peas, field-peas, beans, and even vetches did not apparently require any inoculation. As a rule, they grow on new soils rather vigorously and produced the characteristic nodules, thus indicating that the proper bacteria are present in most soils. It was otherwise with at least two leguminous crops, soybeans and alfalfa. Soybeans, originally introduced into the United States from Japan, did not do very well. They frequently failed to develop that healthy, dark green color characteristic of vigorous leguminous plants. Careful examination showed their roots to be devoid of tubercles. Soybean earth, straw and chaff were obtained from Japan and placed in the ground together with the seed. The plants thus inoculated developed normally and produced an abundance of tubercles.

"This experience demonstrated the need of soil-inoculation for soybeans. Many cases are reported in experiment station literature in which these inoculations gave positive results. For instance, in the experiments of the New Jersey Station, on light sandy soils at Hammonton, when cowbeans and soybeans were planted in the same ground, the former grew luxuriantly and gathered nitrogen from the air by means of their numerous nodules, while the soybeans remained small and yellow and produced no tubercles. It was not until the introduction of some soil from a field where these plants had been grown successfully for several years that the soybeans developed and grew as luxuriantly as did the cowpeas.

"Similar observations were made time and again in the case of alfalfa. Soils to which this crop was new usually required inoculation, even though they had successfully produced red or crimson clover. It appeared, as in the case of soybeans, that the bacteria capable of producing nodules on alfalfa were absent, as a rule, from soils in which this crop had not been raised before. This observation has led to the rather common practice of scattering old alfalfa soil on new fields where this plant was to be established. It was found subsequently that the bacteria causing nodule-formation on alfalfa were seemingly identical with those producing tubercles on sweet clover. Inoculation was therefore superfluous on soils to which sweet clover was native, and, moreover, sweet clover soil could be used as inoculating material for new alfalfa fields."

"*Bacterial activities and money losses.*—The extent of the monetary losses involved in the improper control of the bacterial activities in manure may be appreciated from the following considerations. Taking the amount of manure

and litter for each cow at 15 tons annually and for each horse and mule at 5 tons annually, we find, in round numbers, 130 pounds and 50 pounds of nitrogen respectively to be credited to each animal. With a value of only 8 cents per pound, this nitrogen would be worth $10.40 and $4 respectively. With, say, 60,000,000 of cattle and 20,000,000 horses and mules in the United States, the value of the manurial nitrogen would be greater than $700,000,000. Assuming that the difference between economical and wasteful transformation of this nitrogen in the manure pile by bacteria would represent 20 percent, the monetary loss would amount to $140,000,000."

"A microscopical examination by Grotenfelt of the dirt particles in unstrained, freshly drawn milk revealed the presence of the following substances:

1. Manure—particles (numerous).
2. Fodder—particles (had not passed through the alimentary canal of the animals).
3. Molds and other fungi.
4. Cow hair (numerous).
5. Particles of the skin.
6. Human hair.
7. Parts of insects.
8. Down from birds.
9. Small wooden pieces, shavings, and pieces of fir leaves.
10. Woolen threads.
11. Linen threads.
12. Soil particles (rather frequent) and moss.
13. Fine threads (most likely cobwebs).

"The miscellaneous solid impurities that fall into the pail or milk can act as carriers of germs. Everything being equal, the greater the amount of dirt in the milk, the greater the numbers of bacteria present, and the less satisfactory the keeping quality of the milk. Sanitary dairies make proper allowance for this fact in that the animals are frequently cleaned, the floors and walls are not permitted to accumulate filth, and the udder of the cow is wiped with a moist cloth or sponge shortly before milking. By these means, the number of germs that may be detached from the cow's body during milking is reduced to a minimum."

"These interesting experiments show strikingly that with the exercise of extreme care the milking-machines may prove an adequate means for the production of sanitary milk with good keeping quality. They demonstrate no less strikingly that in the ordinary dairy, and, for that matter, in the best of dairies, the milking-machine may prove a detriment rather than an advantage to the production of high-grade milk. They again emphasize the fact that the elimination of bacteria from dairy utensils is a matter of some difficulty, calling for patience and intelligence on the part of the dairyman."

"When properly carried out, pasteurization reduces the germ content of milk from many thousands or even millions, to a few hundreds or less. Herein lie the advantages and disadvantages of pasteurization, as will be seen from the following considerations: Under normal conditions, milk gradually turns sour on account of the rapid development in it of the lactic-acid bacteria, and the accumulation of lactic acid. The lactic-acid bacteria find no difficulty in

crowding out the other forms, and, while the souring milk is, in itself, objectionable to the dairyman and the consumer, it is, none the less, a protection against the growth of other germs whose products may not be as harmless.

"The lactic-acid bacteria do not produce spores, and are all destroyed in the process of pasteurization. The spore-bearing decay bacteria are now given a free field, and when the temperature conditions are favorable, they multiply rapidly and produce unpleasant tastes and odors in the milk. The substances thus produced from the casein and albumin may prove more or less harmful, and at times, decidedly poisonous.

"Although pasteurized milk cannot always be regarded as wholesome, it can be made a valuable aid in the supply of good milk to the city populations. The disease bacteria are destroyed in the process and the intestinal diseases among children are materially reduced in consequence. Moreover, the keeping quality of the milk is improved, a point of vast significance in the great cities where the milk is frequently twenty-four to thirty-six hours old when it reaches the dealer.

"The conclusions to be drawn from this and similar experiments is that pasteurization is effective for the destruction of disease bacteria in milk and for the improvement of its keeping qualities. It is agreed that city children fed on pasteurized milk, properly heated and properly cooled, are less subject to intestinal disturbances than children fed on raw milk. At the same time it must be admitted that the pasteurization of milk already filled with bacteria, and the products of their activities, will not remedy its defects. The undesirable substances formed by the bacteria were not entirely destroyed by the heating and may still cause injury to the person consuming the milk.

"By resorting to pasteurization, a dealer may be able to dispose of milk that would otherwise quickly become unsalable. Similarly, the failure to cool the pasteurized milk quickly, and to keep it at a temperature of 50°, or below that, may lead to the rapid multiplication in the milk of germs producing injurious or poisonous substances. Hence, pasteurized milk should be consumed within twelve hours or should be immediately cooled down to between 45° and 50°. The intelligent use of pasteurizing apparatus, and the intelligent treatment of the milk subsequent to pasteurization, cannot but prove a decided benefit to all city populations, and particularly to those whose sources of supply are distant."

While the book is an uncommonly good one in most respects, it must be admitted that there is an occasional tendency to what seems an unnecessary repetition, as in Chapters XVIII and XX. At times the author makes a definite statement on one page and then modifies it radically a little later as in the chapter on fallowing. *Wilder D. Bancroft*

The Evolution of Forces. *By Gustave LeBon. 12 × 19 cm; pp. xv + 388. New York: D. Appleton & Company, 1908.*—The author has previously postulated that all matter is continually in a state of dissociation and decay. In this volume he defends the thesis that the atom is a great reservoir of energy and the source of most of the forces of the universe. The first hundred pages are devoted to an exposition of the new principles under the captions: the new bases of the physics of the universe; the irreducible magnitudes of the universe;

the dogma of the indestructibility of energy; the new conception of forces. The remainder of the work is devoted to the problems of physics and the main headings are: the dematerialization of matter and the problems of electricity; the problems of heat and light; the problems of phosphorescence; black light; forces of unknown origin, and hidden forces.

The author's attitude in regard to matter, energy and the ether is shown in the following quotation from p. 13:

"It now seems, however, that physicists should have seen a long time ago —that is, long before the recent discoveries—that matter and the ether are intimately connected, that they are unceasingly interchanging energies, and are in no way two separate worlds. Matter continuously emits luminous or calorific radiations, and can absorb them. Down to the absolute zero it radiates continuously—that is to say, it emits ethereal vibrations. The agitations of matter propagate themselves in ether, and those of the ether in matter, and without this propagation there would be neither light nor heat. The ether and matter are one thing under different forms, and we cannot put them asunder. If we had not taken as a starting point the narrow view that light and heat are imponderable agents because they appear to add nothing to the weight of bodies, the distinction between the ponderable and the imponderable, to which scholars attach so much importance, would long ago have vanished.

"The ether is doubtless a mysterious agent which we have not yet learned to isolate, but its reality is manifest, since no phenomenon can be explained without it. Its existence now seems, to several physicists, more certain than even that of matter. It cannot be isolated, but it is impossible to say it cannot be seen or touched. It is, on the contrary, the substance we most often see and touch. When a body radiates the heat which warms or burns us, what constitutes this heat, if it be not the vibrations of the ether? When we see a green landscape on the ground glass of a camera obscura, what constitutes this image, if it be not the ether?

"The theory of the dissociation of matter has not only served to clear away the two great dichotomies, force and matter, ponderable and imponderable, which seems established forever. The doctrine of the vanishing of matter by its transformation into energy carries with it important consequences in regard to current ideas of energy."

On p. 16, the author enunciates the following as his fundamental principles:

"1. Matter, hitherto deemed indestructible, slowly vanishes by the continuous dissociation of its component atoms.

"2. The products of the dematerialization of matter constitute substances placed by their properties between ponderable bodies and the imponderable ether—that is to say, between two worlds hitherto considered as widely separate.

"3. Matter, formerly regarded as inert and only able to give back the energy originally supplied to it, is, on the other hand, a colossal reservoir of energy—intra-atomic energy—which it can expend without borrowing anything from without.

"4. It is from the intra-atomic energy liberated during the dissociation of matter that most of the forces in the universe are derived, and notably electricity and solar heat.

"5. Force and matter are two different forms of one and the same thing.

Matter represents a stable form of intra-atomic energy: heat, light, electricity, etc., represent unstable forms of it.

"6. By the dissociation of atoms—that is to say, by the materialization of matter, the stable form of energy termed matter is simply changed into those unstable forms known by the names of electricity, light, heat, etc. Matter, therefore, is continuously transformed into energy.

"7. The law of evolution, applicable to living things, is also applicable to simple bodies; chemical species are no more invariable than are the living species.

"8. Energy is no more indestructible than the matter from which it emanates."

While discussing Mayer's failure to get people interested in the doctrine of the conservation of energy, the author says, p. 40:

"The critical mind is so rare a gift that the most profound ideas and the most convincing experiments exercise no influence so long as they are not adopted by scholars enjoying the prestige of official authority.

"Nevertheless, it always happens in the long run that a new idea finds a champion in some scholar possessing this prestige, and it then rapidly makes its way. As soon as the grandeur of the idea of the conservation of energy was introduced by one such, it had an immense success."

On p. 59 we find an interesting criticism of potential energy.

"However this may be, the faculty which physicists have arrogated to themselves of considering the energy which appears to be lost as having passed into the potential state, will always remove the principle of the conservation of energy from experimental criticism. Latent potential energy plays the part of those "hidden forces" by the intervention of which the early mechanics succeeded in fitting into its equations the experiments which escaped them. The moment conservation of energy is admitted as a postulate, we must suppose that that which appears lost is to be found somewhere else, and the abyss of potential energy provides it with an inviolable shelter. But if we start from the contrary postulate, that energy can be used and lost, we are compelled to acknowledge that the second postulate would have in its favor at least as many facts as the first.

"These are, moreover, barren discussions, since experiment is incapable of throwing light on this question. We had, therefore to retain the principle of the conservation of energy until, after having penetrated further into the intra-atomic universe, it has been clearly set forth in what way energy becomes lost. This is a point of which the solution can be dimly seen, and I will presently examine it.

"It would be equally useless to dwell on facts which agree very badly or not at all with the principle of the permanence of energy, since it is enough to imagine any hypothesis whatever to make them fit in with the principle. Thus a way of explaining how the mass of a body can immensely increase with its velocity, as has been proved by experients with radio-active particles, will certainly be found. It has indeed been explained how a permanent magnet may be for an indefinite space of time traversed by currents without its becoming heated by the friction, which would lead to the loss of its magnetism. It was enough to suppose that ether had no resistance—that is to say, to confer

on it a property that the non-instantaneous nature of the propagation of light proves not to exist.

"These universal hypotheses have always allowed a theory to be saved so long as it is a fertile one. Many hypotheses in physics, such as that of the kinetic theory of gases, would probably quickly vanish if experiment could throw light on them. These molecules unceasingly hustling against each other with the velocity of a cannon ball, without becoming heated, thanks to an elasticity supposed to be infinite, have perhaps but a very remote resemblance to the reality. The theory is rightly retained because it is a fruitful one, and because no possible experiment enables us to prove its inaccuracy."

On p. 64, there is a comment on the belief that energy takes different forms appearing as mechanical, electric, calorific and chemical energy.

"It is easy to comprehend the origin of this theory, but when we go deeper into it, we discover neither the necessity nor the exactness of it. All that can be said in its favor is, that it escapes the test of the experiment. It is certain that the various forms of energy appear to transform themselves, or better, that from any form of energy others can be produced. But these are merely apparent transformations like the turning of money into goods. For a five-franc piece we obtain a metre of silk; but nobody thinks that the silver of which the coin is made transforms itself into silk. Yet a like transformation is admitted when we are assured that the friction of a rod of resin with a strip of flannel has been turned into heat and electricity. The modern theory of the equivalence and the transformation of energies seems indeed to be only an illusion arising from the fact that in order to measure them, we have chosen the same unit, *viz.*, that of work estimated in kilogrammeters or in calories."

On p. 72, there is an interesting illustration of the conditions under which energy can be made available.

"Thus, then, without an alteration of level of ether or of matter there can be no possible manifestation of energy. If the sun possesses throughout its mass a uniform temperature of 6000 degrees, and there could exist in it beings capable of supporting that heat, it would represent to them no energy. Having no cold bodies at their disposal, they could produce no fall of heat, a condition indispensable for the production of thermal energy.

"Let us suppose now, that instead of finding themselves at a uniform temperature of 6000 degrees, these imaginary beings live in a world of ice at the uniform temperature of zero, but possess in a corner of their world still colder an unlimited provision of liquid air. Contrary to those plunged in a medium at 6000 degrees they would find in the blocks of ice around them a considerable source of energy. By plunging these latter, in fact, into the liquid air at —180°, they would obtain a considerable alteration of temperature. At the contact of the ice, which is to liquid air a very hot body, this latter would immediately boil, and its vapor could be employed to put motors in operation. The inhabitants of that world would therefore replace the coal of our steam engines by blocks of ice, which they would consider, certainly with more reason than we do coal, reservoirs of energy.

"With this ice and this liquid air, it would be very easy for them to produce the highest temperatures. The tension of the vapor obtained could be employed, in fact, to drive dynamos, by means of which can be obtained electric currents

capable of producing temperatures sufficient to fuse and volatilize all metals."

The author's conception of matter appears in the following quotation, p. 79.

"Bodies are constituted by a collection of atoms, each composed of an aggregate of rotating particles, probably formed by vortices of ether. By reason of their velocity these particles possess an enormous kinetic energy. According to the way in which their equilibria are distributed they generate different forces—light, heat, electricity, etc.

"It is probable that matter owes its rigidity only to the rapidity of the rotary motion of its elements, and that if this movement stopped it would instantaneously vanish into ether without leaving a trace behind. Gaseous vortices, animated by a rapidity of rotation of the order of that of the cathode rays, would in all probability become as hard as steel. This experiment is not realizable, but we can imagine the results by noting the considerable rigidity which is acquired by a fluid animated by great velocity.

"Experiments made in hydro-electric factories have shown that a liquid column only 2 centimeters in diameter, falling through a tube of the height of 500 meters, cannot be broken into by a violent blow from a sabre. The arm is stopped as if by a wall when it arrives at the surface of the liquid. Professor Bernard Brunhes, who witnessed this experiment, is persuaded that if the velocity of the liquid column were sufficient, a cannon ball would not go through it. A layer of water a few centimetres thick, animated by a sufficient velocity, would be as impenetrable to shells as the steel plates of an ironclad.

"Let us give to the above column of water the form of a vortex-ring, and we shall get an image of the particles of matter and the explanation of its rigidity.

"This enables us to understand how the immaterial ether, when transformed into small vortex-rings animated by sufficient velocity, may become very material. It will be also understood that, if these whirling movements were stopped, matter would instantaneously vanish by return to the ether."

On p. 99, the author formulates the following proposition:

"Energy is not indestructible. It is unceasingly consumed, and tends to vanish like the matter which represents one of its forms."

On p. 118, the author discusses one method of transforming matter.

"When we rub a body, when we place it under the influence of an electrified source, or when we subject it to any sort of disturbance of the ether, such as a luminous ray, we are doing quite a different thing to transforming (as the text-books teach) movement or any other energy into electricity. We do not, thus, effect a transformation, but a liberation of forces. We simply dissociate matter by bringing suitable reagents to bear upon it. Electricity is one of the manifestations of this dissociation.

"The magnitude of the intra-atomic energy being, as I have shown, immense, it will be understood that from a very infinitesimal portion of matter there may issue a very large quantity of electricity. This emission is considerable, but is not infinite; and it is probable that if the above experiment were continued for several centuries, we should see the aluminum become gradually less by its conversion into electricity, and finally disappear. We should then have witnessed the complete transformation of matter into energy.

"The experiment on electrification by influence described in this chapter realizes this evolution exactly. We might have read it in the elementary facts which have been before the eyes of physicists for several centuries without their understanding their import.

"It further results from this experiment that electricity, which is one of the products of the dissociation of matter, is at the same time one of the most active agents of this dissociation. It constitutes by its special attractions for the elements of matter one of those appropriate reagents of which the importance has been shown in a chapter of my earlier work. It is one of those against which matter is defenseless, while it is able to strive against very energetic but not appropriate reactions.

"The irresistible power of attraction of a minute particle of electricity dissociates matter which the impact of a shell might pulverize and even volatilize, but could not dematerialize."

A new possibility in war is suggested on p. 149:

"The problem of sending a pencil of parallel Hertzian waves to a distance possesses more than a theoretical interest. It is allowable to say that its solution would change the course of our civilization by rendering war impossible. The first physicist who realizes this discovery will be able to avail himself of the presence of an enemy's ironclads gathered together in a harbor to blow them up in a few minutes, from a distance of several kilometers, simply by directing on them a sheaf of electric radiations. On reaching the metal wires with which these vessels are nowadays honeycombed, this will excite an atmosphere of sparks which will at once explode the shells and torpedos stored in their holds.

"With the same reflector, giving a pencil of parallel radiations, it would not be much more difficult to cause the explosion of the stores of powder and shells contained in a fortress, or in the artillery parks of an army corps, and finally the metal cartridges of the soldiers. Science, which at first rendered wars so deadly, would then at length have rendered them impossible, and the relations between nations would have to be established on new bases."

The study of the action of light on metals led to the following conclusions, p. 221:

"Again I had to proceed by successive eliminations, and I at last succeeded in verifying that the metals lost under the influence of heat something which they could afterwards regain by repose. This something was simply a small provision of radio-active particles formed spontaneously in all bodies. As the final result of these researches I reached the two following conclusions: (1) Light, especially the ultra-violet rays, which only exercise, as is known, an insignificant calorific action, dissociates matter and transforms it into products analogous to those emitted by radium or uranium; (2) outside the action of light, and independently of it, luminous or dark heat provokes in bodies the loss of an infinitesimal quantity of the radio-activity they contain, which may be spontaneously regenerated. All bodies are therefore slightly radio-active, and the dissociation of matter is indeed a universal phenomenon.

"Ramsay has very thoroughly observed in his skilful experiments, this 'fatigue' of metals, which lose their properties more or less after a certain time. He attributes it to a modification of the equilibrium of the atoms on their surface, a theory which, however, does not sensibly differ from mine."

Experiments on the rate of decay of the phosphorescence of a calcium sulphide screen led to the following remarks, p. 241:

"The general appearance of the above curve shows, indeed, that things happen as if the reaction exciting the phosphorescence placed itself in equilibrium with an opposing force acting in a converse direction. Immediately after its insolation, the screen contains an excess of phosphorescence. Under the influence of the opposing force, this excess is dissipated, rapidly at first, then slowly when the moment approaches when the equilibrium is established between the phosphorescence and the opposing force. When this equilibrium is attained, the reactions which produce the phosphorescence stop entirely. The opposing force being unable to act further on the reaction which generated the phosphorescence, the body will retain its residue of phosphorescence until a rise in temperature again destroys the equilibrium.

"I do not know of what this opposing force consists. I can only say that things take place exactly as if it existed. This interpretation has also led me to the discovery of the phenomena of invisible phosphorescence studied in a future chapter."

On p. 258, the author sums up certain conclusions as follows:

"From the above considerations may be deduced the following laws, applicable to all bodies phosphorescent by light or by heat:

"1. There are no bodies phosphorescent without heat. A body capable of being rendered phosphorescent by light will only manifest its phosphorescence at a certain temperature.

"2. For each phosphorescent body there is a miminum temperature below which, exposure to the light cannot produce visible phosphorescence.

"3. To each temperature correspond a certain emission of phosphorescence which cannot be exceeded.

"4. Bodies which heat renders phosphorescent also become so by light, but only slightly. They differ from these visibly phosphorescent by light only that in these last the luminous rays entirely regenerate the whole of the destroyed phosphorescence instead of regenerating only a part of it."

The chapters on invisible phosphorescence and on photography through opaque bodies are extraordinarily interesting. The last page, p. 318, of the latter chapter is worth quoting in full.

"All the experiments set forth in this chapter based on the use of bodies sensitive to radiations of great wave-length, but this sensitiveness is only very great for radiations hardly exceeding 3μ. Now those emitted by bodies at a relatively low temperature—the human body, for example—are of much greater wave-length, and do not impress phosphorescent matter. If we could discover a body sensitive to those radiations, nothing would be easier than to photograph a living body in the dark without any other source of light than the invisible light it is continuously emitting.

"Down to the absolute zero of temperature, all bodies incessantly radiate, as has been seen, waves of light invisible for our eyes, but probably perceptible by the animals called nocturnal and capable of finding their way in the dark.

"To them, the body of a living being, whose temperature is about 37° C, ought to be surrounded by a luminous halo, which the want of sensitiveness of our eye alone prevents our discerning. There do not exist in nature, in reality,

any dark bodies, but only imperfect eyes. All bodies, whatever, are a constant source of visible or invisible radiations, which, whether of one kind or the other, are always radiations of light."

These lengthy quotations give a fair idea of the range and character of the book. It is probable that very few people will agree with the author on all points; but that does not make the book any the less interesting. The author has discovered a number of important and unexpected facts, and he does make one think. Those two things are more than enough to make us overlook any looseness of argument which we may detect here and there. The translation is not a good one though one perhaps should not call it distinctly bad. *Wilder D. Bancroft.*

The New Physics and its Evolution. *By Lucien Poincaré. Being the authorized translation of "La Physique Moderne, son évolution." 12 × 19 cm; pp. vi + 344. New York: D. Appleton & Company, 1908.*—The headings of the chapters are: principles; the various states of matter; solutions and electrolytic dissociation; the ether; wireless telegraphy; the conductivity of gases and the ions; cathode rays and radio-active bodies; the ether and matter; the future of physics.

The author begins by pointing out that the developments in physics during the first decade of the twentieth century have not been a bit more startling than those during the first decade of the nineteenth century. He next discusses the mechanical view of phenomena in which, p. 11, the idea of Descartes is treated as an ideal to be reached sooner or later.

"Certain scholars—particularly those of the English School—outrunning experiment, and pushing things to extremes, took pleasure in proposing very curious mechanical models which were often strange images of reality. The most illustrious of them, Lord Kelvin, may be considered as their representative type, and he has himself said: 'It seems certain to me that the true sense of the question, Do we or do we not understand a particular subject in physics? is—Can we make a mechanical model which corresponds to it? I am never satisfied so long as I have been unable to make a mechanical model of the object. If I am able to do so, I understand it. If I cannot make such a model, I do not understand it.' But it must be acknowledged that some of the models thus devised have become excessively complicated, and this complication has for a long time been discouraged by all but very bold minds. In addition, when it becomes a question of penetrating into the mechanism of molecules, and we were no longer satisfied to look at matter as a mass, the mechanical solutions seemed undetermined and the stability of the edifices thus constructed was insufficiently demonstrated."

On p. 19, in the chapter on measurements there is another interesting quotation from Lord Kelvin.

"I often say," Lord Kelvin has said, "that if you can measure that of which you are speaking and express it by a number you know something of your subject; but if you cannot measure it nor express it by a number, your knowledge is of a sorry kind and hardly satisfactory. It may be the beginning of the acquaintance, but you are hardly, in your thoughts, advanced towards science, whatever the subject may be."

On p. 63, in the chapter on the principles of physics, we find the following:

"By experiments which are now classic, it becomes established that the quantity of heat thus created independently of the nature of the bodies is always (provided no other phenomena intervene) proportional to the energy which has disappeared. Reciprocally, also, heat may disappear, and we always find a constant relation between the quantities of heat and work which mutually replace each other.

"It is quite clear that such experiments do not prove that heat is work. We might just as well say that work is heat. It is making a gratuitous hypothesis to admit this reduction of heat to mechanism; but this hypothesis was so seductive, and so much in conformity with the desire of nearly all physicists to arrive at some sort of unity in nature, that they made it with eagerness and became unreservedly convinced that heat was an active internal force.

"Their error was not in admitting this hypothesis, it was a legitimate one since it has proved very fruitful. But some of them committed the fault of forgetting that it was an hypothesis, and considered it a demonstrated truth. Moreover, they were thus brought to see in phenomena nothing but these two particular forms of energy which in their minds were easily identified with each other."

An interesting instance of pragmatism appears in the chapter on the ether, p. 179.

"Fresnel founded his theory of double refraction and reflexion by transparent surfaces, on the hypothesis that the vibration of a ray of polarized light is perpendicular to the plane of polarization. But Neumann has proposed, on the contrary, a theory in which he recognizes that the luminous vibration is in this very plane. He rather supposes, in opposition to Fresnel's idea, that the density of the ether remains the same in all media, while its coefficient of elasticity is variable.

"Very remarkable experiments on dispersion by M. Carvallo prove, indeed, that the idea of Fresnel was, if not necessary for us to adopt, at least the more probable of the two; but apart from this indication, and contrary to the hypothesis of Neumann, the two theories, from the point of view of the explanation of all known facts, really appear to be equivalent. Are we then in presence of two mechanical explanations different indeed, but nevertheless both adaptable to all the facts, and between which it will always be impossible to make a choice? Or, on the contrary, shall we succeed in realizing an *experimentum crucis*, an experiment at the point where the two theories cross, which will definitely settle the question?

"Professor Wiener thought he could draw from his experiment, a firm conclusion on the point in dispute. He produced stationary waves with light polarized at an angle of 45°, and established that, when light is polarized in the plane of incidence, the fringes persist; but that, on the other hand, they disappear when the light is polarized perpendicularly to this plane. If it be admitted that a photographic impression results from the active force of the vibratory movement of the ether, the question is, in fact, completely elucidated, and the discrepancy is abolished in Fresnel's favor.

"M. H. Poincaré has pointed, however, that we know nothing as to the mechanism of the photographic impression. We cannot consider it evident

that it is the kinetic energy of the ether which produces the decomposition of the sensitive salt; and if, on the contrary, we suppose it to be due to the potential energy, all the conclusions are reversed, and Neumann's idea triumphs.

"Recently a very clever physicist, M. Cotton, especially known for his skilful researches in the domain of optics, has taken up anew the study of stationary waves. He has made very precise quantitative experiments, and has demonstrated, in his turn, that it is impossible, even with the spherical waves, to succeed in determining on which of the two vectors which have to be regarded in all theories of light on the subject of polarization phenomena the luminous intensity and the chemical action really depend. This question, therefore, no longer exists for these physicists who admit that luminous vibrations are electrical oscillations. Whatever, then, the hypothesis formed, whether it be electric force or, on the contrary, magnetic force which we place in the plane of polarization, the mode of propagation foreseen will always be in accord with the facts observed."

In the chapter on radio-active bodies we find the following passages, p. 287.

"The most prudent physicists and those most respectful to established principles may, without any scruples, admit the explanation of the radio-activity of radium by a dislocation of its molecular edifice. The matter of which it is constituted evolves from an admittedly unstable initial state to another stable one. It is, in a way, a slow allotropic transformation which takes place by means of a mechanism regarding which, in short, we have no more information than we have regarding other analogous transformations. The only astonishment we can legitimately feel is derived from the thought that we are suddenly and deeply penetrating to the very heart of things.

"But those persons who have a little more hardihood do not easily resist the temptation of forming daring generalizations. Thus, it will occur to some that this property, already discovered in many substances where it exists in more or less striking degree, is with differences of intensity, common to all bodies, and that we are thus confronted by a phenomenon derived from an essential quality of matter. Quite recently, Professor Rutherford has demonstrated in a fine series of experiments that the α particles of radium cease to ionize gases when they are made to lose their velocity, but that they do not on that account cease to exist. It may follow that many bodies emit similar particles without being easily perceived to do so; since the electric action, by which this phenomenon of radioactivity is generally manifested, would, in this case, be but very weak.

"If we thus believe radioactivity to be an absolutely general phenomenon, we find ourselves face to face with a new problem. The transformation of radioactive bodies can no longer be assimilated to allotropic transformations, since, thus, no final form could ever be attained, and the disaggregation would continue indefinitely up to the complete dislocation of the atom. The phenomenon might, it is true, have a duration of perhaps thousands of millions of centuries, but this duration is but a minute in the infinity of time, and matters little. Our habits of mind, if we adopt such a conception, will be none the less very deeply disturbed. We shall have to abandon the idea so instinctively dear to us that matter is the most stable thing in the universe, and to admit,

on the contrary, that all bodies whatever, are a kind of explosive decomposing with extreme slowness. There is in this, whatever may have been said, nothing contrary to any of the principles on which the science of energetics rests; but an hypothesis of this nature carries with it consequences which ought in the highest degree to interest the philosopher, and we all know with what alluring boldness M. Gustave Le Bon has developed all these consequences in his work on the evolution of matter."

In the chapter on the ether and matter, the following paragraphs, p. 296, are of especial interest.

"Unfortunately, if a gas is not absolutely incapable of emitting some sort of rays by simple heat, the radiation thus produced, no doubt by reason of the slightness of the mass in play, always remains of moderate intensity. In nearly all the experiments, new energies of chemical or electrical origin come into force. On incandescence, luminescence is superposed; and the advantage which might have been expected from the simplicity of the medium vanishes through the complication of the circumstances in which the phenomenon is produced.

"Professor Pringsheim has succeeded in certain cases, in finding the dividing line between the phenomena of luminescence and that of incandescence. Thus, the former takes a predominating importance when the gas is rendered luminous by electrical discharges and chemical transformations, especially, play a preponderant rôle in the emission of the spcetrum of flames which contain a saline vapor. In all the ordinary experiments of spectrum analysis the laws of Kirchhoff cannot, therefore, be considered as established, and yet the relation between emission and absorption is generally tolerably well verified. No doubt we are here in presence of a kind of resonance phenomenon, the gaseous atoms entering into vibration when solicited by the ether by a motion identical with the one they are capable of communicating to it."

From the final chapter on the future of physics, the following paragraphs, p. 324, are worth quoting.

"The electron has conquered physics, and many adore the new idol rather blindly. Certainly we can only bow before an hypothesis which enables us to group in the same synthesis all the discoveries on electric discharges and on radioactive substances, and which leads to a satisfactory theory of optics and of electricity; while by the intermediary of radiating heat, it seems likely to embrace shortly the principles of thermodynamics also. Certainly one must admire the power of creed which penetrates also into the domain of mechanics and furnishes a simple representation of the essential properties of matter; but it is right not to lose sight of the face that an image may be a well-founded appearance, but may not be capable of being exactly superposed on the objective reality.

"The conception of the atom of electricity, the foundation of the material atoms, evidently enables us to penetrate further into nature's secrets than our predecessors; but we must not be satisfied with words and the mystery is not solved when, by a legitimate artifice, the difficulty has simply been thrust further back. We have transferred to an element ever smaller and smaller, those physical qualities which in antiquity were attributed to the whole of a substance; and then we shifted them later to those chemical atoms which, united together, constitute this whole. To-day we pass them on to the electrons which

compose these atoms. The indivisible is thus rendered, in a way, smaller and smaller, but we are still unacquainted with what its substance may be. The notion of an electric charge which we substitute for that of a material mass will permit phenomena to be united which we thought separate, but it cannot be considered a definite explanation or as the term at which science must stop. It is probable, however, that for a few years still physics will not travel beyond it. The present hypothesis suffices for grouping known facts, and it will doubtless enable many more to be foreseen, while new successes will further increase its possessions.

"Then the day will arrive when, like all those which have shone before it, this seductive hypothesis will lead to more errors than discoveries. It will, however, have been improved, and it will have become a very vast and very complete edifice which some will not willingly abandon; for those who have made to themselves a comfortable dwelling-place on the ruins of ancient monuments are often too loth to leave it."

This is a good book. The author has selected his material well and has presented it in a satisfactory form. Unfortunately, the unknown translator has done his work very badly. Such foot-notes as the one on p. 25 make one wonder how much the nameless editor has understood of the book he was supposed to edit. *Wilder D. Bancroft.*

Qualitative Analyse vom Standpunkte der Ionenlehre. *By Wilhelm Böttger. Zweite, umgearbeitete und stark erweiterte Auflage. 16 × 24 cm; pp. xvi + 524. Leipzig: Wilhelm Engelmann, 1908. Price: paper, 10 marks; bound, 20 marks.*—The first edition was reviewed (6, 267) in 1902. The arrangement of the second edition differs to a certain extent from that of the first, the special and the general parts now being kept separate. The book is divided into the following sections; general principles; manipulation; characteristic reactions of the cations and their salts; scheme of qualitative analysis for cations; scheme of qualitative analysis for anions; preliminary tests in qualitative analysis; dissolving and leaching of solids for qualitative analysis; rare elements.

It is perhaps a question whether this book is suitable for an introductory course in qualitative analysis; but it would unquestionably be useful for a more advanced course and it is a book which every one interested in chemistry should look through at some time or other. Some of the experiments in the section on general principles are admirable. As instances of this, I cite the action of cobalt salts on hypochlorites, p. 109; the filtration of silver chlorides, p. 116; the testing of a potassium chrome oxalate solution for potassium, chromium and oxalate ions, p. 89. *Wilder D. Bancroft*

Kurzes Lehrbuch der organischen Chemie. *By William A. Noyes. Mit Genehmigung des Verfassers ins Deutsche übertragen von Walter Ostwald und mit einer Vorrede von Wilhelm Ostwald. 14 × 21 cm; pp. xxiv + 722. Leipzig: Akademische Verlagsgesellschaft m. b. H., 1907.*—The interesting feature of this book is that the author has dropped the usual distinction between aliphatic and aromatic compounds. He treats all the hydrocarbons together, then all the alcohols and phenols, and so on. This is unquestionably a logical arrangement; but so was the old arrangement. It seems to the reviewer that the treatment adopted in this book is not a good one for elementary students. Take toluene

as an instance. The behavior of hydrogen in the side chain is different from that of the so-called ring hydrogen. The properties of benzyl bromide and the bromtoluenes differ radically. It is easier for the student to grasp these distinctions if he has the general characteristics of the aliphatic series before he starts in on the aromatic compounds. On the other hand, this book will be a valuable aid to the advanced student. It is not only desirable but important to look at any subject from as many different view-points as possible. This book gives us a new one for organic chemistry and is therefore valuable. As an elementary text, it will probably not achieve a great success.

Wilder D. Bancroft

The Electric Furnace, *its Evolution, Theory and Practice. By Alfred Stansfield. 15 × 23 cm; pp. xi + 211. New York: Hill Publishing Company, 1907. Price: $2.00 net.*—This is an unpretentious book which does very well what it sets out to do. The subject is treated under the following heads: history of the electric furnace; description and classification of electric furnaces; efficiency of electric and other furnaces, and relative cost of electrical and fuel heat; electric furnace design, construction and operation; production of iron and steel in the electric furnace; other uses of the electric furnace; future developments of the electric furnace.

It makes comparisons quite simple to remember that one ton of good coal will produce approximately the same quantity of heat as one kilowatt year, p. 33. On p. 35 there is a very instructive diagram showing the heat utilized and wasted in crucible steel furnaces, in reverberatory furnaces, in open-hearth furnaces, in shaft furnaces, and in electric furnaces. The section on materials of furnace construction is good and so is that on the production of heat in electric furnaces, while the one on the production of iron and steel in the electric furnace is better still. In the chapter on other uses of the electric furnace the author takes up the ferro alloys, graphite and the carbides, electrothermal production of zinc, silicon, quartz, alundum, nitric acid, phosphorus, carbon bisulphide, the Acker process, sodium, and aluminum.

The chapter on the future developments of the electric furnace is so interesting that I quote the following paragraphs from it:

"Until a few years ago the electric furnace was a wonderful and expensive commodity, and the idea of using it for heating on a commercial scale was preposterous. About 13 tons of coal were needed to produce one electrical horse-power for a year, and this electrical energy would furnish less heat than one ton of the original coal. Such a method of using coal was evidently extremely wasteful. The greater efficiency of electrical heating somewhat reduces this difference, and together with the smaller cost of water-power has made it cheaper in some cases to use 'white coal' instead of black, in the furnace.

"In comparing the supplies and prices of coal and electrical energy, it should be remembered that one ton of good coal produces as much heat as 1½ horse-power years of electrical energy, but that the efficiency of the electrical furnace is from 2 to 30 times as great as the efficiency of ordinary metallurgical furnaces, so that an electrical horse-power year will produce as much effective heat as several tons of coal.

"The world's production of coal at the present time is about 1,000 million

tons a year, and is steadily increasing. The electric furnace draws its energy mainly from water-powers. The water-powers of the world that have already been utilized are very small in comparison with the present coal output, having in all only about 1 per cent of the heating power of the latter.

"In view of the fact that coal mining is a long-established industry, while the electrification of water-powers is only of recent growth, it is reasonable to suppose that the latter will increase more quickly in proportion than the former. In both cases there are limits, however; the coal mines will ultimately all be discovered and worked out to a depth at which the cost becomes almost prohibitory, while on the other hand the water-powers will all be developed, leaving only those that are too expensive to utilize. When these limits are reached the coal supply will have sunk to a small proportion of the amount needed for heating and power, but the water-powers will continue to give a steady supply of power for all time with only maintenance and interest charges.

"The exhaustion of coal supplies may not be reached for hundreds or thousands of years, but if the development of the mines proceeds, as at present, at increasing rates like compound interest, their practical depletion may be less distant than now appears probable. In any case it seems likely that as coal can only be used once, while water-powers are not deteriorated by use, the latter may be expected ultimately to largely replace the former for motive power and to some extent for furnace work.

"The present age, especially on this continent, is one of the barbaric use of the mineral assets such as coal and ore. As the population increases and the development of mines is pushed to its limit, the increasing scarcity both of the ore and of the fuel to smelt it, will make it necessary to spend more money in utilizing these to the very best advantage, using the coal with the greatest economy and extracting every possible product from the ore. It has been suggested that the present enormous production of iron and steel for example can only represent a temporary condition, that of extracting the iron from its ore. When most of the iron ores have been converted into iron or steel our descendants will have to be content to use over again the metal so produced, merely making good the deficiency caused by rusting and the increase in population. Iron is, however, a very plentiful metal, forming perhaps 4 or 5 percent of the earth's crust, and the coal will last for a large number of years, but the time must come when it would be extravagant to use coal, mined at great expense, for the mere production of heat. As coal becomes more scarce it will be used for its chemical properties of reducing iron and other metals from their ores, while the necessary heat would be produced electrically. At that time Canadians may have to heat their houses electrically, or if, on account of the large population in Canada at that time, such methods of heating were too expensive, they may have to live underground during the winter.

"In the more immediate future there will no doubt be a great development of electrical power, which may in consequence replace coal to some extent in furnace operations such as the production of steel and iron from certain ores, and in certain localities; on the other hand, the rapidly increasing market for electrical power will tend to keep the price from falling, relatively to the price of coal, and it is therefore unlikely that coal and coke will be at all largely replaced for smelting purposes by the electric current for many years to come.

"When the possibilities of the electric furnace have been more fully ascertained it is likely that some large water-powers that are situated conveniently with regard to metallic ores may be utilized for their reduction, the electric plant being available for other purposes after the exhaustion of the ore supply. At the present time such a large return can be obtained from capital in Canadian industries that only the most easily developed water-powers are considered. When the country becomes more thickly settled and when capital is more abundant, a smaller return will be expected and the interest charges on permanent developments such as hydro-electric plants will be less, thus enabling powers to be utilized that would be too costly under present conditions."

There are one or two places where a change would have been an improvement. The reviewer believes that the original Cowles furnace was an arc furnace and not a resistance furnace, p. 6. It is doubtful whether we are justified in saying that calcium is an intermediate product, p. 10, in the conversion of lime into calcium carbide. It is quite possible that it is. The behavior of silica makes such an assumption plausible, but the facts hardly warrant the definite statement that "the lime is reduced by means of the coke to the metal calcium, and this in turn reacts with more coke to form a carbide." On p. 159 the cut of de Laval's zinc furnace is upside down. On p. 186 it seems a pity that we should not have one of the drawings of the aluminum furnace which came out during the lawsuit between the Pittsburg Reduction Co. and the Cowles Co. *Wilder D. Bancroft*

Chemisch-optische Untersuchungen. *By J. H. Jellett. (Oswald's Klassiker der exakten Wissenschaften. No. 163). Übersetzt von L. Frank. Herausgegeben von W. Nernst. 12 × 19 cm; pp. 83. Leipzig: Wilhelm Engelmann, 1928. Price: bound, 1.60 marks.*—Probably every man, who lectures on physical chemistry, makes at least a passing reference to Jellett and his work on the optical rotation of the alkaloids. Doubtless a few out of that large number have read Jellett's original paper, but certainly most of them have not. To both groups of men this translation of Jellett's paper will be welcome.

Wilder D. Bancroft

Über die Oxydation des Stickstoffes im gekühlten Hochspannungsbogen bei Minderdruck. *By Adolf Koenig. 17 × 24 cm; pp. 76. Halle: Wilhelm Knapp, 1908. Price: paper, 3.00 marks.*—With a long arc under ordinary conditions, the equilibrium depends on the thermal equilibrium. With a short arc playing under diminished pressure in a cooled tube an electrical equilibrium must be reached because the percentage of 9.8 NO actually obtained corresponds to the improbable temperature of over 4300° C. With a gas mixture of approximately 82% oxygen and 18% nitrogen, a yield of over 12% NO was obtained, corresponding to an estimated equilibrium temperature of about 5000° C. Since the values were higher, the more slowly the gas passed through the tube, it is quite impossible that the equilibrium can have depended on thermal conditions alone. Full details in regard to this very creditable piece of work are given in the pamphlet. *Wilder D. Bancroft.*

THE ELECTROCHEMISTRY OF LIGHT. V

BY WILDER D. BANCROFT

The Problem of Solarization. Part II

A summing-up of the problem of solarization from a single point of view has recently been given by Lüppo-Cramer.[1] While one may not, and probably will not, agree with all that Lüppo-Cramer says, the presentation is an interesting one and therefore is given at length.

"The oxidation theory of solarization assumes that the substance of the latent image, formed by a brief action of light, is oxidized by the oxygen of the air to a difficultly reducible substance. This theory is not only insufficient but also *hopelessly absurd* as far as it is applied to silver bromide. It is quite remarkable that the oxygen of the air should oxidize the *resistant sub-bromide* in the short period necessary for solarization in intense light especially when we remember that the same sub-bromide forming the latent image is so indifferent in the dark to oxygen and even to strong oxidizing agents.

"That the assumption of the participation of the oxygen of the air in the solarization process is untenable, can be demonstrated by quite simple experiments. Guthrie[2] announced that silver chloride blackens under benzene exactly as it does in air. The fact that the blackening of silver chloride under naphtha takes place just as it does in the air was cited by Carey Lea as an argument against the view that the blackening in light has anything to do with oxidation. I have extended these experiments and have found that silver bromide, silver chloride, mercurous bromide and mercurous iodide gelatine films show no difference in photochemical behavior when exposed under benzene, alcohol or ether. Also the solarization of ordinary silver bromide gelatine

[1] Photographische Probleme, 138 (1907).

[2] Eder's Jahrbuch der Photographie, 5, 417 (1891).

is not affected in the slightest by benzene, alcohol and ether.[1]

"The improbability of the oxidation hypothesis in regard to solarization appears also from the self-evident *continuity* in the action of light on silver bromide where there is not the slightest evidence that the substance of the normal latent image differs qualitatively[2] from that of the latent solarized image. On the contrary it appears that there is a *continuous splitting-off of bromine*, which is proved by the appearance of the directly visible image which every one knows cannot be reversed.

"The effect of reducing agents in preventing solarization has already been cited by Abney in favor of the oxidation theory; but we are really dealing with the power of these substances to absorb halogen and not with their reducing power. In a polemic against Carey Lea in 1878, H. W. Vogel[3] brought out sufficiently the difference between the reducing action and the ability to absorb halogen. In opposition to Carey Lea's conception of sensitizers as reducing agents, Vogel cited silver nitrate which is unquestionably an oxidizing agent and yet which is the best of all sensitizers on account of its strong absorptive power for the halogens.

"My guess, that a similar state of things would hold true for solarization, has been confirmed completely by the experimental evidence. Dry plates were bathed for one minute in one percent solutions of nitrite, sulphite, hydroquinone, ethylene diamine, as well as in a solution containing one percent silver nitrate and two percent citric acid. The plates were dried, exposed for a few minutes to daylight along with check plates under a negative, washed, and developed with metol-soda. While the check plates, which had not been bathed, gave good, completely reversed solarization images, the solarization was completely eliminated on the

[1] A *short drying* of the plate exposed under the liquids is sufficient to insure a perfectly satisfactory development.

[2] Cf. Luther: Archiv. wiss. Photographie, 1, 273; 2, 35.

[3] Phot. Mittheilungen, 14, 140.

plates which had been soaked in the above-mentioned solutions. *The best results were obtained with the plate which had been saturated with silver nitrate.* This gave a relatively good diapositive[1] while the film which had been treated with the other substances had not passed completely beyond the 'neutral state.'

"Solarization is therefore eliminated most completely by silver nitrate acidified with citric acid, which consequently contained *free nitric acid* and is certainly to be looked upon as an *oxidizing agent* rather than a reducing agent.

"There can be no question but that the action of these so-called 'reducing' agents such as nitrites, sulphites, developer substances, etc., on the one hand, and that of the soluble silver salts on the other hand, depends on the one thing common to all, the power of absorbing halogen. Of all the 'sensitizers' which cause a much more rapid reduction of silver bromide by light because they take up bromine, and which prevent solarization in spite of this much stronger reduction, the nitrites are the best suited to furnish a clear explanation of the phenomenon.

"If dry plates are dipped for about two minutes in a two percent solution of sodium nitrite and are then dried, they will be found to change more in a few minutes' exposure to diffused daylight than the unsoaked check plates after several hours' exposure to direct sunlight. The action of the nitrite can be followed very nicely on 'microscopically thin' films. Even with the longest exposure, pure films show no certain change of the single grains when examined under microscope. On the other hand, in the films containing nitrite there can soon be noticed a darkening of the grain beginning at the edge and gradually working inward. After about an hour's exposure to daylight the *whole grain is blackened* while the original crystalline silver bromide grain appears rent in many places, apparently the result of small bromine explosions from within.

[1] That silver nitrate checks solarization in silver bromide collodion has recently been confirmed by Eder, Photochemie, 287 (1906).

"I may also add that a nitrite bath after the exposure has no effect on the development of the plate and also that the presence of nitrite *during* the exposure only produces an effect in the stages of very great over-exposure. With a ten-fold exposure, for instance, the nitrite acts exactly as in a normal exposure, *i. e.*, the image appears as though exposed for a somewhat shorter time.

"The action of sensitizers in a solarizing exposure consists therefore unquestionably in bringing about a much greater reduction and in eliminating the solarization in the subsequent development.

"Abney[1] found that the grain in the upper layer of a solarized film is finer than in a normally exposed film. This observation is unquestionably right; the fact can be recognized by the surface shine on a plate which has been exposed to solarization and then developed.

"In view of the importance which the question of a difference in the size of the grain in solarized films would probably have for the still failing explanation of solarization, I have made some more experiments under different conditions which yielded different results.

"In Abney's investigations and in all the more recent ones, experiments were also made with silver bromide films of normal thickness, which were developed as a whole and from which thin films were prepared for the microscopic study, either by direct cutting as Abney did, or by dissolving the reduced film and pouring the dilute emulsion again.

"It is easy to get a large number of silver bromide grains approximately in one plane if one makes a sufficiently thin film of silver bromide gelatine at the start, by diluting the ordinary emulsion with five to ten parts of water and then by throwing off most of the emulsion after pouring, as is done in making Lippmann plates.[2]

"If such thin films are exposed once normally, *i. e.*,

[1] Eder's Jahrbuch der Photographie, 12, 394 (1898).

[2] Valenta: Photographie in natürlichen Farben, 53 (1906).

long enough to produce an intense blackening of the whole film, and are exposed another time to solarization, *i. e.*, about five to fifteen minutes in bright daylight, and are then developed for one to two minutes with metol-soda, the effect of different illuminations and exposures is shown chiefly in differences in the number of the grains and not in differences in the sizes. The photomicrographs are especially instructive if the plates are only washed and not fixed after development, in which case the silver bromide grains originally present, which are easily distinguishable from the reduced grains, remain and can never serve as landmarks.

"Fig. 17[1] shows the normally exposed and Fig. 18 the solarized half of a plate prepared by the above method (magnification about 1000 diameters). In Fig. 18 there are a very large number or unreduced grains while in Fig. 17 there are only a few scattered ones. The scattered blackened grains on the solarized plate do not differ distinctly in size from those in Fig. 17. The state of the grain in the solarized plate is thus quite similar to that of chemical fog. As an instructive instance of the grain of fog, I show in Fig. 19 the photomicrograph of a thin plate which has been developed without being exposed. Here one has again the most convincing proof that chemical fog affects certain grains only and that the others are unaffected by it even when apparently in direct contact.

"Fig. 19 is not directly comparable with Fig. 17 and Fig. 18 because another emulsion was used as can easily be seen from the distinctly crystalline form of the grain. Nevertheless it brings out sufficiently the similarity that both fog and solarization are phenomena affecting only part of the grains in a film. In other words, the solarizing exposure decreases the possibility of reducing the silver bromide and the resulting blackening of the few grains represents only the blackening of the originally fogged grains. The apparently greater fineness of the grains in solarized films and the

[1] [The cuts referred to in the text are not reproduced in this article.]

surface shine are therefore to be referred to the fact that when there are large numbers of reduced grains these grow more and that thereby larger aggregates of grains are formed in the deeper layers to which the light does not really reach. When the number of grains is small, as at the solarized surface, the grains do not coalesce.

"The investigation of solarization phenomena in these very thin films seems especially important for the reason that diffusion phenomena[1] cannot seriously be brought forward to account for all sorts of occurrences in the thin films.

"In general, therefore, one cannot speak of an essentially different size of grain in films which have been solarized and then developed. On the other hand, the size of the original silver bromide grain has a great deal to do with the formation of the solarization image. This is quite striking with collodion emulsions, which, as I mentioned[2] some years ago, never show so characteristically complete a reversal as do the ordinary dry plates.[3] Experiments with silver bromide gelatine diapositive plates show that the binder as such is not the determining factor nor yet the lesser thickness of the film which results from the properties of collodion. The fine-grained silver bromide gelatine plates (*D*) used for these experiments had about one-sixtieth the sensitiveness of the very sensitive Schleussner "Specially Rapid Plates" (*S*) of 16°–17° Scheiner.

"But while the plate "*S*" gave an excellent, good-printing, solarized duplicate after exposure to daylight for thirty seconds under a negative, the plate "*D*" gave no satisfactory negative regardless of whether the exposure was under the calculated time of 60 x 30″ = 30′ or whether the plate was exposed from half an hour up to several days.

[1] In regard to the so-called tanning theory of solarization, see Lüppo-Cramer, Wiss. Arbeiten, 44 (1907); Eder, Photochemie, 308 (1906). Weisz, Zeit. phys. Chem., **54**, 334 (1906).

[2] Phot. Correspondenz, **1901**, 350; also Lüppo-Cramer: Wiss. Arbeiten, 41 (1902).

[3] For reasons that will be given later, the greater tendency of silver iodide to solarize introduces a different state of things with "wet plates."

There were always slight traces of solarization it is true, the uncovered edges of the plate for instance always developing somewhat less than those portions which were very heavily covered in the original negative. The difference in the behavior as compared with that of plate "*S*" is of fundamental importance. Silver bromide gelatine plates with an *extraordinarily* fine grain, such as the Lippmann plates, show no normal solarization phenomena at all even when they have been exposed so long that the direct photochemical change is distinctly visible after a preliminary fixing.[1] Silver chloride gelatine plates act in the same way.

"The method of examining the grain, in which the film was poured very thin, permitted the examination of the photographic change with the grains all in a single plane and proved very useful for the study of the phenomenon of solarization. It is exactly in solarized films that it is important to recognize that the processes in the upper layers may be different from those in the lower ones. One needs only recall the experiment of Vidal[2] who gave very strongly overexposed plates a surface fixing and thus brought them into a state in which they developed normally. I recall also my experiment with bromine water and gelatine plates[3] whereby the upper layers lost the power of developing.

"When we have the grains all in one plane we can study solarization in its simplest form; and, under these conditions, as we have already seen, the continued action of light (solarization) entirely destroys the reducibility of the single grains of silver bromide. We can also check and eliminate solarization in various ways. A comparison of Fig. 21 with Fig. 20 shows the action of nitrite when there is a solarizing exposure. While the plate containing no nitrite is completely solarized, the presence of nitrite prevents the solarization absolutely. Every grain of silver bromide is reduced by the silver developer. Exactly the same result can be obtained

[1] See p. 189.
[2] Bull. Soc. Franç, 1898, 282; Phot. Correspondenz, 1904, 122, 213.
[3] Lüppo-Cramer: Wiss. Arbeiten, 107 (1902).

by impregnating the film with silver nitrate, because this salt is a halogen absorber just like nitrite and the others. The action of the silver nitrate is however not quite so satisfactory as that of the nitrite because impregnating the film with silver nitrate causes the unexposed portions to fog to a certain extent. This shows under the microscope as an increase in the fogged grains. The characteristic elimination of solarization by silver nitrate, as described by me, is of course not affected by these side-issues.

"The elimination of an existing solarization by suitable reagents can also be followed very well by examining the grain. Thus Fig. 23 shows the action of Eder's chromic acid and nitric acid mixture[1] on the solarized film. Plate 7 was treated for fifteen minutes with chromic acid and, after being washed, was developed together with the solarized check plate, Fig. 22. It is clear that chromic acid has changed most of the solarized grains into the state in which they can be reduced by the developer.

"A third method of eliminating solarization, if one may so speak, is by a preliminary fixing. It has long been known that solarization also occurs when the plate is developed physically. Sterry has also stated that the *solarized image remains solarized* even after a preliminary fixing or, as he puts it, 'that the latent organic image is capable of a reversal.' Eder[2] has also observed that the solarized image on silver bromide collodion remains partially solarized after a preliminary fixing. The author also sometimes obtained partial reversals after a preliminary fixing exclusively with the extraordinarily fine-grained films to which reference has been made, and which did not solarize when developed normally. With ordinary very sensitive dry plates my experience was like that of Kogelmann[3] for I never obtained solarization after a preliminary fixing even though the exposure lasted several days. The same result was obtained whether the

[1] Eder: Phot. Correspondenz, **1902**, 647.
[2] Photochemie, 312 (1906).
[3] Kogelmann: Isolierung der Substanz des latenten Bildes, 23 (1894).

acid metol strengthener is used, or the mixture recommended as a developer by Neuhauss[1] which works very slowly. The microscopic examination of a number of experiments confirmed the view that with the larger amounts of silver left after a solarizing exposure and a preliminary fixing there are also a great many more grains which develop physically to where they can be seen under the microscope than is the case with normal illumination.

"Since my previous investigations[2] have shown that silver and silver bromide remain as a solid solution after a preliminary fixing and that the reactions of the photochemical decomposition products depend to a very great extent on the size of the original grain, the explanation of the puzzling phenomena of solarization will be found when we know more about the nature of the solutions of silver in silver bromide. At present we have absolutely no data on the subject.

"The action of halogen-absorbing agents under a solarizing illumination leads us naturally to the assumption that the bromine set free by the light is the cause of the reversal of the image. This hypothesis has been often expressed, most explicitly by Hurter and Driffield as well as by Sterry. These investigators agree in assuming that the change which gives a normal latent image capable of development is merely a molecular re-arrangement and that the bromine set free by further illumination checks the development and finally causes solarization by preventing development.[3] Sterry[4] also discards the oxidation theory as an explanation for the action of sensitizers in preventing solarization but curiously enough he assumes that they act 'by returning the bromine.' Thus he writes in No. 5 of his conclusions: 'When the conditions permit of part of the halogen being returned either directly or from the gelatine, development is greater, and the tendency to reversal is delayed.'

[1] Phot. Rundschau, **1898**, 257; **1905**, 54.
[2] Photographische Probleme, 62 (1907).
[3] Hurter and Driffield: Phot. Jour., **22**, 150 (1898)
[4] Ibid., **22**, 264 (1898).

"Luggin[1] has also expressed himself very clearly to the effect that the relatively large amount of 'sub-salt' resulting from an intense exposure with the accompanying increase in halogen pressure prevents the silver bromide from forming nuclei on which the metal can deposit. Luggin also emphasizes the fact that the use of suitable sensitizers is the most effective means of keeping the *bromine pressure as low as possible* and thus of preventing solarization. Luggin therefore suggests the same explanation as that which followed from my experiment with the film impregnated with silver nitrate. It seems to me that Luggin's explanation fits in well with my experiment that solarization phenomena are more marked the larger the grain. Another fact that fits in well is that of the ready solarization of silver iodide.[2] Silver iodide gelatine solarizes markedly long before there is a direct visible blackening probably because here much lesser amounts of halogen are sufficient to give the halogen pressure necessary for reversal.

"Silver chloride gelatine is a most striking instance of the opposite extreme. A normal image, free from any sign of reversal, can be developed or strengthened either by chemical or physical development even when the plate has been exposed to the direct action of a very intense light.

"It is appropriate now to consider a phenomenon which is undoubtedly related to the reversal caused by a solarizing exposure, but which is based on a different photochemical reaction. It is the observation made by Lassaigne[3] in 1839 and afterwards studied by Abney that silver chloride films, which have been blackened by light, are decolorized by bathing in an iodide solution so that one can copy drawings direct as positives. Recently Hrudnika[4] has put this reaction into a practical form. The process can be carried out very easily with ordinary celloidin paper which is allowed to become

[1] Eder's Jahrbuch der Photographie, 12, 162 (1898).
[2] Phot. Correspondenz, 1903, 614.
[3] Eder's Handbuch der Photographie, 2nd Ed., 2, 80.
[4] Phot. Correspondenz, 1903, 35, 544.

quite black, then washed and dipped in a slightly acid solution of potassium iodide. The reaction depends on the decomposition of hydriodic acid by light and on the great readiness with which iodine reacts with the silver sub-salt. In comparison with the behavior of the bromine salt, this reaction furnishes an analogy for the difference between silver bromide and silver iodide in regard to solarization and to the decay of the latent image.[1] Iodine has a much greater tendency to combine with the sub-salt than has bromine. For this reason Lassaigne's reaction takes place much more slowly with bromides.

"Luggin states 'that the beginning of solarization can often be checked by using smaller stops and a correspondingly longer exposure.' This is confirmed admirably by the behavior of silver iodide gelatine with which solarization depends to a tremendous extent on the intensity of the light. Those who believe in the theory of gelatine as a sensitizer should notice that the effect of nitrite in preventing solarization is not neutralized by the gelatine. It is obvious that the bromine which is set free does not pass at all beyond the sphere of attraction of the silver bromide grains. It is precisely similar to the disappearance of the action of light on mercurous bromide[2] where my experiments showed that the bromine set free by the light converted the grain into its original state and therefore could not have reacted chemically with the gelatine.

"The reactions of the solarized latent image with oxidizing agents are quite surprising but similar to those described[3] in connection with the 'destruction' of the latent image. It is well known that the reversal of the latent image is accompanied by a relatively strong chemical change which is *visible before the development.* The so-called photobromide (Carey Lea) which is then formed is completely insoluble in concentrated nitric acid and also is quite resistant to other

[1] Phot. Correspondenz, 1904, 402.
[2] Ibid., 1904, 404.
[3] Lüppo-Cramer: Photographische Probleme, 112 (1907)

oxidizing agents such as persulphate, bromine water, etc. If a film is exposed till solarized, treated with oxidizing agents and then developed, the solarized image changes to a normal one. Given the relatively large amount of chemically changed substance which results from the solarizing illumination of the silver bromide grains, it is possible by means of oxidizing agents to change the surface of the grain so much that the development takes an entirely different course, while the interior of the grain offers so great a resistance to the attack of the silver-solvent that the loss of substance cannot be detected at all directly and is only slightly perceptible when development follows a preliminary fixing.

"The solarization is forced back to a much greater extent if one adds a small amount of a solvent for silver bromide to the reagents which dissolve silver, the reason being that the attack penetrates further into the grain. I attained this by adding a sulphocyanate to Eder's chromic acid mixture or still better by adding it to a suitably diluted nitric acid.[1]

(*a*) 200 cc water + 40 cc nitric acid, sp. gr. 1.4.

(*b*) Solution *a* + 10 cc potassium sulphocyanate, 1 : 5.

"Six strongly solarized Warnerke sensitometer scales were soaked in these solutions for (1) five minutes, (2) ten minutes, (3) twenty minutes and then washed thoroughly. On all, the directly visible blackening remained unchanged so far as one could judge by the light of the dark room. With chemical development traces of solarization were still visible on 1*a*, while clear powerful normal images were obtained from 2*a* and 3*a*. With the plates which had been soaked in solution *b*, the forcing back of the solarization was much more marked. The images, which also develop normally, are much weaker than those from solution *a*. On the plate which had been twenty minutes in the solution, the normal development of five minutes with metol-soda brought out only slight traces of an image. In spite of this, as a result of the photobromides, development after fixing brought out

[1] The plates used for this purpose were hardened before exposure by drying with chrome alum.

an image of the entire scale which even with 3*b* was only slightly weaker than that on a check plate.

"The phenomenon of solarization, therefore, when considered as a whole, presents a large number of unsolved problems. One is nevertheless justified in assuming that the action of light on silver bromide consists in a *continuous setting-free of bromine* from the point at which the plate can first be developed up to the most complete solarization, and that no secondary processes, such as the action of the oxygen of the air or the action of the medium need to be considered in the explanation. In fact the second reversal of the solarization is very probably to be explained solely as a photochemical decomposition of silver bromide.

"It was shown by Janssen[1] in 1880 that the ordinary state of solarization is followed by a second reversal which gives rise to a 'negative of the second order.' Since then, the phenomenon has been noticed a number of times. On the other hand the brothers Lumière did not obtain the second reversal with silver bromide gelatine even when they exposed 18480000000 times as long as was necessary to obtain an ordinary negative. Now it is not at all surprising that one might fail to obtain such a complicated phenomenon as this second reversal of the image since it depends on the sum of the chemical processes occurring in the *numerous superposed layers of grains* constituting the normal thickness of the silver bromide film. As we have already seen, the principle underlying the first reversal is that the light actually sets free a relatively large amount of bromine and destroys completely the reducibility of each single grain for normal conditions of development. Since the visible change produced by light increases continuously with ever-increasing exposure, a plausible explanation of the second reversal of the image would be that no grains in the film are reduced by the developer and that, after fixing, there remained only the visible blackening caused directly by the light.

[1] Eder's Handbuch der Photographie, 2nd Ed.

"Experiments with microscopically thin films convinced me that this hypothesis is false. After the thin films had been exposed from one to five hours the silver bromide grains blackened completely in the developer while the undeveloped single grains showed scarcely a perceptible difference under the microscope as compared with the unexposed grain or with the grain which had been exposed up to the ordinary first solarization and then developed. It is rather remarkable that the form of the developed grains does not differ anything like so much from that of the original silver bromide as does the form of the reduced grain of the negative of the first order.[1]

"With films of normal thickness the second reversal can be obtained very easily if the plate be exposed under a negative to sunlight, a part of the plate being left uncovered. After about one hour's exposure to the direct sunlight, this uncovered edge blackens in the developer much more strongly than any part of the image; but the image itself shows partially the phenomenon of the second reversal, though usually the result is a jumble of mixed images."

Luggin[2] has made quite a study of what he calls solarization photo-currents. Luggin coated a platinum electrode with a silver halide and dipped the resulting silver halide electrode into a solution of the corresponding potassium halide. He then polarized this electrode until it showed definite constant potential differences against a normal calomel electrode. To maintain each potential difference a definite current C was required. This polarizing current was called negative when the silver halide electrode was anode and positive when the electrode was cathode. After Luggin had determined the current density necessary to maintain a certain potential difference in the dark, he exposed the silver halide to a light of definite intensity, and in this case the current necessary to maintain the potential difference had a different value, say $C + c$. The current corresponding to c

[1] Phot. Correspondenz, 1905, 408, Fig. 14 and Fig. 15.

[2] Zeit. phys. Chem., 23, 577 (1897).

was called by Luggin the photo-current. This photo-current was called a *normal* current when it tended to make the silver halide electrode the cathode and a *solarization* current when it tended to produce the reverse effect.

Luggin[1] says that "the phenomenon which I call *photo-electric* solarization can best be observed with electrodes which are brought, before being illuminated, to a potential considerably (for instance 0.1 volt) above[2] the previously determined value of v.[3] If one exposes such an electrode to light, there is usually a positive or, as I shall call it in future, a normal photo-current during the first few minutes. (As I have previously pointed out, the polarization to a high potential usually causes an increase in the equilibrium potential very quickly and this explains the positive current observed at first.) As time goes on this normal photo-current decreases gradually and regularly for perhaps as much as an hour and then changes, sometimes after only a short exposure to light, to a negative current which is often several times as strong as the original normal current. As a matter of fact the normal decomposition of the silver bromide does not cease during the exposure; there is merely added to it an oxidation process which causes a current in the opposite direction, a *solarization* current as I call it. This fact becomes clear if the electrode is brought into the dark again. It may then happen that the solarization current increases since there is an immediate cessation of the normal current which worked against it during the exposure; while it is a peculiarity of the solarization current in every case I have studied that it disappears only *gradually* when the light is cut off.

"The most intense solarization currents are noticed with electrodes which have *never before* been polarized to a high potential. The strengths of the currents are however always

[1] Zeit. phys. Chem., 23, 588 (1893).

[2] [Luggin considers an oxidizing agent to have a higher potential than a reducing agent. A higher potential therefore means increased anodic polarization of the silver halide electrode.]

[3] [v = the equilibrium potential.]

less than the strengths of the normal currents for slightly polarized electrodes. If one keeps the electrode for a long time at a very high potential, the tendency to give a negative current decreases more and more. Such an electrode then shows little more than a weak normal effect. It is possible that the process, which takes place during the continuous polarization of silver bromide in the dark, is to be considered as a kind of solarization. With electrodes polarized to a high potential, the solarization current plays an important part as a disturbing factor, affecting the value of the normal photo-current. The deformation of the c, v curves, noticed with intense lighting, is due in my opinion chiefly to a partial solarization of the light-sensitive layer.

"In this respect we get very instructive results with certain experiments in which the illuminated electrode is on open circuit and consequently cannot give any external photo-current. Such an electrode polarizes higher and higher under the action of light so long as the setting-free of bromine from the light-sensitive layer is not compensated by the loss of bromine due to a spontaneous depolarization. This latter must finally prevail, because the supply of bromine from the silver bromide to the electrode will decrease as the potential is raised more and more above the equilibrium value while the losses will become correspondingly greater. Within certain, perhaps rather narrow, limits these losses might be called proportional to the difference between the value of the natural potential and the value of the potential resulting from the action of light. It is easy to calculate the polarizing effect c on the part of the illuminated film so long as there is no solarization. The same process, which gave the photo-current $c = (v - V)/b$ when the electrode potential V did not vary during the exposure, causes the electrode on open circuit to be polarized to a higher potential. The phenomenon is similar to that which would take place if an electrode at a potential V were connected by a resistance b with an electrode kept constantly at the potential v. The calculated

increase of the potential V with the time of illumination t is given by the formula

$$V = V_{\infty}(1 - e^{-at}),$$

where V_{∞} is the potential attained by the electrode after an infinitely long exposure, and a is a constant. The result is confirmed by experiments with the electrode described in a previous paragraph.

"But the electrodes do not all obey the simple law even for such weak lights as 20 $M^{-2}K$ (meter candles). Usually a variation from the theoretical values becomes noticeable after only a quarter of an hour's exposure to light. The potential of the electrode becomes approximately constant or it begins to sink instead of rising farther. If the electrode is then placed in the dark, the potential does not merely drop to the original value, but goes beyond it. The cause of the disturbance is obviously the solarization process which caused the negative solarization currents with electrodes which had been polarized very strongly. In the experiments with electrodes on open circuit the electrode potential is considerably lower and the solarization phenomenon is therefore not enough to overcome the normal current during the exposure."

"Parallel experiments with silver chloride and silver iodide electrodes give the same qualitative results as the silver bromide electrodes; but both the silver chloride and the silver iodide electrodes show characteristic peculiarities which deserve a more careful discussion because these peculiarities appear also in the actual field of photography.

"Silver chloride was examined both in yellow and in blue light on account of the remarkable behavior of silver electrodes towards the different rays of the spectrum, as described by Becquerel.[1]

"According to Becquerel, a silver electrode covered with silver chloride is sensitive for only the more refrangible rays provided it has not previously been exposed to light. If blue light, however, has once acted on the electrode and has

[1] Ann. Chim. Phys. (3), 9, 263 (1843).

darkened the silver chloride, thereby changing its absorption spectrum, it is then sensitive in a marked degree for yellow and even for red rays. The curve of sensitiveness for such an electrode shows two maxima, the original one in the blue between *G* and *H*, and one in the less refrangible part of the spectrum where the electrode was at first not sensitive. Becquerel did not recognize that this was simply an extension of the region of sensitiveness, resulting from the change in the absorption spectrum. He thought that there were two separate processes, the blue rays starting the photochemical reactions and the red rays continuing them.

"In my experiments I used a platinum electrode covered with electrolytically precipitated silver chloride which had been exposed to light for a time sufficient to make it sensitive to all the rays of the spectrum. The electrode was placed in a N/10 potassium chloride solution. In order to get yellow or blue light I placed, in the path of the beam, glass vessels with plane sides, filled with potassium bichromate or copper ammonium sulphate solution. By a mere chance the sensitiveness was very nearly the same in the two cases. In this case, the *c*, *V* curves are essentially rectilinear even for the strongest lights, though these were not very strong on account of the interposed color filters. In consequence the photo-currents were fairly weak. Near the high potentials for which one would have expected an equilibrium, the curves bend and run approximately parallel to the axis of ordinates ($c = 0$). This behavior is undoubtedly due to a continued displacement of the equilibrium potential as a result of the strong polarization. If one returns to lower potentials, the old values for the photo-currents are obtained with a fair degree of accuracy.

"Under these circumstances an accurate determination of the equilibrium potential is not possible. The form of the lower parts of the curve makes it probable that the equilibrium potential of the silver chloride in the case of moderately polarized electrodes is approximately as high as that of silver bromide under corresponding conditions. For short ex-

posures the curves for yellow and for blue light are so much alike that there is no reason to assume any appreciable difference in the equilibrium potentials for the two kinds of light. So long as we are only considering normal processes, both kinds of light cause decomposition of the same type.

"Yet, in another respect, the silver chloride electrodes behave very differently towards the two kinds of light. In yellow light they show a much greater tendency to solarize than in blue light. Thus it may happen that one obtains a negative current after a long exposure to yellow light while the original, normal, photo-current continues with only a slight diminution when the electrodes are exposed to blue light. With silver chloride electrodes the negative currents also persist after the electrode has been brought back into the dark.

"The special property of the less refrangible rays, that they excite a photo-electric solarization, accounts for a difference between the upper parts of the *c*, *V* curves for yellow and blue light (above + 0.2 volt). These portions of the curves are already convex to the coördinate axes. As was to be expected the convexity is more marked for the yellow light than for the blue, and for the more intense as against the less intense light.

"In respect to the phenomenon of photo-electric solarization, silver bromide therefore has a special sensitiveness differing from that for the normal photo-electric production of an image.

"This effect due to the nature of the light is of great importance for the theory of photo-electric solarization. We are not dealing simply with a reversal of the normal process, taking place because the pressure of the halogen in many parts of the film exceeds the equilibrium pressure corresponding to the equilibrium potential. There is no analogy with the case of heated lime which takes up or gives off carbon dioxide depending on the partial pressure of this gas in the atmosphere. Through the sign of the solarization current we know that an oxidation process is going on, but

it is not certain that it must consist in a taking up of halogen. We are certain however that the solarization process does not form a silver halide identical with the one which we started. We cannot, however, tell at what partial pressure of the oxidizing agent, no solarization takes place; in fact, we cannot even say whether it would be possible to determine an equilibrium potential (perhaps a very low one) for the solarization process by the same method used by which we determine it for the normal process. It is possible that the change which causes the solarization current is not strictly proportional to it and that the current becomes noticeable only after a considerable change has taken place."

"The experiments, previously described, show the significance of the equilibrium potential for the photo-electric decomposition of the silver halides. They also furnish much information as to the values of these potentials for electrodes dipping into solutions of the potassium salts of the corresponding halogens. In the paragraph in which the equilibrium potential was characterized as a number which measured the dissociating tendency of illuminated silver halide, it was pointed out that any such potential value holds only for that particular photochemical change which occurs in the electrolyte under consideration. Even when we are considering the case of a silver bromide electrode in a potassium bromide solution, we are not certain that the bromine pressure of the silver bromide acts exclusively against an external bromine pressure; it may have to work partially against an oxygen pressure. The spontaneous polarization of a highly polarized electrode is due in part to bromine losses resulting from convection currents, and partly to a loss of oxygen. In the dark these convection losses are covered exclusively by the polarizing current; in the light there is also a polarizing action due to the silver bromide. There may also be a partial formation of oxygen and hydrobromic acid instead of a simple setting-free of bromine. It has however been shown previously that the bromine and the oxygen at the electrode surface are to be considered as in equilibrium. The two

reactions therefore correspond to the change in free energy and the complication introduces no indefiniteness in this case.

"If the electrode stood in a solution of an oxygen salt, such as potassium sulphate, instead of in a potassium bromide solution, the formation of hydrobromic acid and oxygen would take place more readily, since the opposing pressure of the bromine ions would be reduced to a minimum. In the sulphate solution one would therefore expect a correspondingly higher value for the equilibrium potential.[1]

"More noticeable is the increase of the equilibrium potential when the bromine substitutes in compounds which have a special tendency to take up halogen. Such is very markedly the case in a bath which contains silver nitrate. Even in N/100 solution with the high electrode potential of +0.42 volt[2] and with an intensity of light of only 20 KM^{-2}, normal photo-currents were obtained continuously with a silver bromide electrode prepared like the one described in a previous paragraph. Silver bromide may thus polarize the electrode to a high potential without a trace of free bromine appearing. At the equilibrium potential it is an oxygen or a nitric acid potential which checks the photoelectric decomposition. (The spontaneous decomposition of the silver bromide of course cannot be prevented by polarization.)

"There is also a very marked displacement of the equilibrium potential when silver iodide electrodes are dipped in a silver nitrate solution.

"It is not possible to make a definite calculation of the equilibrium potential in silver nitrate because it is not possible to tell just what happens to the silver halide when the solution is changed. The experiments in KCl, KBr and KI show in fact that the value of the equilibrium potential may

[1] I made a single experiment with N/10 K_2SO_4 and a silver bromide electrode on open circuit. The form of the curve was practically identical with that previously obtained for N/10 KBr.

[2] Measured against the calomel electrode as zero.

be affected to a great extent by a continuous polarization of the electrode to a high value; this introduces an uncertainty. The phenomenon is presumably connected in some way with the power of the silver halides to take up free halogen. According to Carey Lea,[1] silver iodide takes up iodine readily, in fact to such an extent that a dilute sherry-colored iodine solution may be decolorized thereby. According to the same author,[2] silver chloride carries down the chlorides of other metals and holds them surprisingly fast, while similar results are also obtained in other solutions.

"The essential part played by the equilibrium potential in the photo-electric phenomena shows up in many facts for which people formerly were unable to account.

"For instance, when Becquerel covered silver plates with silver halides and exposed them under solutions of neutral salts, he always obtained positive (normal) photo-currents except with many of his silver iodide electrodes. Under these circumstances, it is not a sufficient explanation to say that in these cases the silver iodide reacts with the underlying silver.[3] If one remembers however, that the equilibrium potential of silver iodide is lower than the potential of the calomel electrode and that the potential of silver in potassium chloride is approximately that of the calomel electrode, there is no further reason to be surprised at the phenomenon.[4]

"Another example shows how the photo-electric efficiency changes with a change in the electrolyte in which the electrode stands. Chaperon and Mercadier[5] found that silver

[1] Am. Jour. Sci., **33**, 489 (1887).

[2] Ibid., **34**, 385 (1887).

[3] Becquerel: La Lumière, **2**, 129.

[4] Especially noteworthy is the statement that with thin silver iodide films the lighted electrode is the anode, while it is the cathode when the silver iodide layer is a thick one; in other words, thin films give normal photo-currents and thick ones solarization currents. It is possible that the solarization takes place chiefly in those portions of the film in which the setting-free of iodine was the most difficult from the start. This is similar to the assumption made in the case of the light-sensitive silver bromide electrodes.

[5] Comptes rendus, **106**, 1595 (1888).

electrodes coated with silver sulphide are especially sensitive to red and infra-red light, that they always give negative (solarization) currents,[1] and that they are effective in all salt solutions except those of the alkali sulphides. This becomes intelligible the moment one recalls that solarization currents decrease with falling potential and that silver in silver sulphide has a potential lower by 1.36 volts than silver in N/10 silver nitrate solution.[2]

"The normal photo-currents are usually helped by a lowering of the electrode potential and the solarization currents by a raising of the potential.

"The experiments previously described have shown that the following values are all-important for the normal photochemical change at an illuminated light-sensitive electrode.

(1) The equilibrium potential which is a measure of the tendency of the silver halide to decompose in the light. Its value is determined by the nature of the reaction which takes place when the silver halide gives off halogen in contact with the metal of the electrode.

(2) The potential of the metallic electrode itself which acts as a sort of counter-pressure, checking the decomposition."

Further on in the same paper, Luggin[3] says:

"It has already been pointed out that the photo-electric solarization depends on the nature of the light, that it is much more marked at high potentials than at low potentials, that it increases with the intensity and length of the exposure, and that it usually persists for a while after the exposure is over. I come back to this again in order to show that similar photo-electric phenomena have been obtained before; but the observers did not perceive either the connection with the potential of the electrode or the analogy, which

[1] Rigollot: Comptes rendus, **121**, 164 (1895).
[2] Ostwald: Lehrbuch allgem. Chemie, 2nd Ed., **2**, 1, 982
[3] Zeit. phys. Chem., **23**, 606 (1893).

I am going to point out later, with the well-known solarization phenomena in photography.

"Hankel[1] observed some very remarkable phenomena with copper electrodes which were still covered with the oxide film resulting from rolling or which had been browned by being heated for a long time at 150°.

"When exposed under a blue glass to sunlight, these plates gave normal currents which remained normal even during long exposures. When exposed under green and yellow glasses, these plates gave rise to currents in the opposite direction, which became weaker as time went on and which even changed their sign in some cases, so that weak normal currents were produced. When the light was cut off, there was either an increase in the normal current already flowing, or a change from the weak negative current to a distinctly normal current. In the cases studied by Hankel it was the negative [positive?] current which increased in intensity with length of exposure, which continued after the exposure, and which therefore appears as a sort of secondary phenomena.

"Minchin[2] observed a similar secular change in the normal currents with silver electrodes dipped in eosine or fluoresceine solutions. Currents were obtained which were negative during the first moments of exposure but which soon became positive and which increased still further when the light was cut off.

"It seems to be very often the case that reduction and oxidation processes take place simultaneously at an illuminated, light-sensitive electrode. According to my experiments, solarization is not to be prevented completely either by continuous polarization to a high potential or by an intense preliminary exposure. On the other hand the results, which have been obtained as to the change of the solarization currents with the time, give us a method of limiting the effect

[1] Ber. sächs Ges. Wiss., **27**, 298 (1875). Becquerel observed something similar with silver plates coated with red photochloride; Ann. Chim. Phys. (3), **32**, 176 (1851).

[2] Phil. Mag. [5], **31**, 207 (1891).

of this disturbance even at high potentials and with intense illumination, while we can correct for the initial disturbance by following the changes over a relatively long period of time. There would be no especial difficulty in shortening the time for some of the experiments to a fraction of a minute and in thus decreasing very much the solarizing action even of quite intense lights. The very sensitive methods of the indirect measurement of the current take but very little time when used as a zero method. At the moment of exposure one would have to make such a change in the polarizing electromotive force as just to balance the polarizing effect of the photo-current on the electrode. In many cases it would also be possible to make observations by reading the first throw of the galvanometer, a method which was used by Rigollot[1] with great success in his experiments on the effect of the spectrum on light-sensitive electrodes. It would only be necessary to neutralize the deflection of the galvanometer needle by the polarizing current, just before the exposure, by means of a magnet or by means of a coil through which such a current flowed as would bring the needle to the zero position.

"Variations in temperature are also disturbing factors because they affect the polarizing current, but errors due to this cause are diminished by decreasing the time necessary for an observation.

"Owing to the high light-sensitiveness of the silver halides, the light-sensitiveness of the smooth metallic electrode is not of much importance so long as the potentials are low. Becquerel states that a carefully cleaned platinum surface is not light-sensitive at all, while Hankel says that the sensitiveness of a smooth platinum electrode becomes less the more thoroughly the metal is cleaned. It must also be remembered that, with electrodes covered with a halide salt, only a fraction of the incident light actually reaches the metal. In spite of this it would be desirable to have parallel

[1] Ann. Chim. Phys. (6), 22, 567 (1891). Comptes rendus, 121, 164 (1895).

experiments with smooth electrodes polarized to high potentials."

"The parallelism [between the photo-electric and the photochemical phenomena] is not yet at an end. In the field of photochemical reactions we find a strict analogy with the negative photo-currents which are superposed on the normal photo-currents at high electrode potentials and which finally become the more important.

"It has been observed that the silver halides become darker during the first stage of the exposure but that they become lighter again if the exposure is prolonged. This phenomenon is called solarization by the photographers. Abney[1] made a careful study of it and found that it was conditioned on the presence of oxidizing agents.

"Herschel was the first to observe the reversal of a photochemical action as the result of a more prolonged exposure. He prepared a silver iodide paper with an excess of silver nitrate, exposed it to light until it was blackened, and soaked it in a solution of potassium iodide, whereupon a further exposure to light made the previous image disappear. When the experiment was repeated by Abney, it appeared that the reversal took place when the solution had an acid reaction and not an alkaline one. This is quite natural because iodine is set free much more readily from hydriodic acid than from potassium iodide. Consequently the iodine pressure of the acid solution (which could be determined at a platinum electrode) is very much greater than that of the alkaline solution. To observe the same phenomenon with silver bromide or silver chloride an oxidizing agent must be added.

"Potassium permanganate, bichromate, nitric acid, hydrogen peroxide and ozone all act in the same way. All the rays of the spectrum are capable, under certain conditions, of neutralizing a previous action of light, but the solarizing action of the red rays is much greater than that of the blue.

[1] Proc. Roy. Soc., **27**, 291, 451 (1878). Phil. Mag. [5], **5**, 61 (1878); **10**, 200 (1880).

"Abney also showed that no bleaching takes place in presence of reducing liquids or gases.

"Now one should notice the agreement between the conditions under which Abney obtains solarization and the conditions under which I observed the negative photo-currents. In both cases a high pressure of the oxidizing constituents was necessary and in both cases the phenomena were obtained more readily with silver iodide than with silver chloride or silver bromide. In view of all this, I feel that I am justified in calling the negative currents solarization currents. The solarization currents and the photochemical solarization phenomena stand in the same relation, one to the other, as the normal photo-currents and the normal blackening of the image when a picture is copied photographically.

"The tendency of the silver chloride electrode to solarize especially readily in yellow light finds its analogy in some well-known phenomena from the field of photography. With the exception of the Becquerel[1] heliochromes, which owe their existence to stationary waves,[2] all the directions for making silver chloride heliochromes require such a treatment of the silver chloride as to make solarization phenomena probable. The dry silver halide is exposed for an extraordinarily long time to the action of an intense, colored light,[3] so that a high pressure of the oxidizing substances may be assumed. (A long exposure of a paper[4] silvered with silver nitrate causes finally a high pressure of the oxidizing agent owing to the decomposition of the silver nitrate.) The same result is obtained much more easily by adding an oxidizing agent to the silver chloride after it has become dark violet in the light, and then exposing the silver chloride again to colored light. This method was first described by Poitevin[5] and gives pic-

[1] Ann. Chim. Phys. (3), **22**, 451 (1848); **25**, 447 (1849).

[2] Zenker: Die Photochemie (1868). Wiener: Wied. Ann., **55**, 224 (1895). Lippmann: Comptes rendus, **112**, 274 (1891).

[3] Seebeck: Goethe's Farbenlehre, **2**, 716.

[4] S. Flaurent: Phot. Arch., **1891**, 307.

[5] Comptes rendus, **61**, 1111 (1865).

tures in which the whites are reproduced properly, while the white in the Seebeck process always has the well-known dark color of silver chloride which has been exposed for a long time to light. According to Poitevin any oxidizing agent will do; but potassium bichromate[1] gives rather the best results.

"The brightening of the dark photochloride takes place first in the less refrangible portions of the spectrum, which are the ones first to show their colors (infra-red is not considered). In photochromy therefore the yellow and red light is especially able to cause an oxidation of the silver chloride.[2] This is precisely analogous to what was observed with light-sensitive silver chloride electrodes.

"It is possible that the photo-electric phenomena may be of great importance for just this branch of photography. According to Wiener,[3] Poitevin's process gives the best results when the substance is kept moist. It must be possible therefore to realize the colors with light-sensitive electrodes dipping in salt solutions. There could be no real difficulty in determining the potentials at which the single colors came out best and purest. Then one would have to find the potentials for which the spectrum was best reproduced as a whole and the potentials at which the single colors were changed by light. Judging from the published directions for silver chloride photochromy it would probably be better to expose the electrodes in a solution of oxygen salt rather than in a chloride solution."

Scholl[4] has made some very interesting observations

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[1] There is also copper sulphate in the bath, but the object of this addition is not entirely understood. Krone assumes the formation of colored copper and chromium compounds. Krone: Darstellung der natürlichen Farben durch Photographie (1894); Eder's Jahrbuch der Photographie, **6**, 333 (1892).

[2] Chastaing was the first to point out the peculiar oxidizing action of the less refrangible rays and he cited an extraordinary number of cases in illustration of it. Ann. Chim. Phys. (5), **11**, 145 (1877).

[3] Wied. Ann., **55**, 224 (1895).

[4] Ibid., **68**, 163 (1899).

on the part played by oxygen when silver iodide is exposed to light.

"In order to get a clear understanding of the processes taking place at the surface of silver iodide under the influence of light, it is desirable to simplify the conditions as much as possible and to use silver iodide plates which are not in contact with metallic silver. After a satisfactory explanation has been obtained for the phenomena occurring under these conditions, it will be desirable to extend the experiments to silver iodide films in contact with silver plates.

"When a glass plate is covered with silver and then exposed to iodine vapor until all the silver has been changed into silver iodide, the plate will be found to be covered with a perfectly clear yellowish film of silver iodide which soon becomes opaque[1] if exposed to an intense light. This raises the question as to *what the reaction is which causes the clouding and what the opaque substance is.* It can be shown that silver chloride loses chlorine when exposed to light and it seems reasonable to expect a corresponding change when the silver iodide is exposed to light. If iodine passed out of the silver iodide into the air, the volume of the solid mass would be smaller and cavities might be formed which would make the film appear opaque. The cloudy substance would then be a sub-iodide. On this hypothesis there could be no clouding if the silver iodide film were covered with a layer impenetrable to iodine which would thus keep the iodine from escaping.

"Silver iodide plates were prepared with an excess of iodine and then covered in places with collodion, with an alcoholic solution of shellac or with potash water glass. When exposed to a powerful, white, electric light the protected portions showed no or almost no changes, while the un-

[1] Schultz-Sellack [Pogg. Ann., 143, 442 (1871)] states that a marked clouding occurs only if iodine is present in excess and that it does not appear if the plate is treated, before exposure, with reducing vapors, such as sulphur dioxide, or with liquids which absorb iodine. I found that the clouding could be avoided almost completely if the plate were removed in time from the action of the iodine vapor or if it were freed from the excess of iodine by a gentle heating before the exposure.

protected portions became distinctly cloudy.[1] It made no difference whether the glass side or the film side was exposed to the light, which does away with the objection that the absorption of light by the protecting layer might be a factor. It was also shown that light, which passed through glass plates partially coated with collodion, caused a uniform clouding on underlying silver iodide plates. Since the light was just as effective in the places where it passed through the collodion film as in the places where it did not, it follows that the absorption in collodion is negligible. Since the index of refraction of collodion lies between those of silver iodide and of air, the result of exposing the film side of a silver iodide plate coated with collodion in spots will be that less light will be reflected into the air and more light will pass into the silver iodide at the places covered with collodion than at the bare spots. In spite of this somewhat greater intensity of light, *the change takes place very much more slowly when the surface of the silver iodide is covered.*

"Also if a glass lens with a radius of curvature of about 50 cm is pressed down tight enough, a disc of silver iodide, about 3 mm in diameter, will be protected from clouding while the remaining portions will become quite opaque.

"There was a chance of detecting the iodine set free, in case an illuminated silver iodide film would iodize the surface of an adjacent silver plate. After two glass plates had been covered, one with silver iodide and the other with silver, they were placed with the two layers in contact and were held together by sealing-wax. Half of the glass side of the silver iodide plate was then exposed to light. The silver surface was somewhat changed, but scarcely more so than when the silver was exposed to an equally intense light without any silver iodide being present. No distinct interference colors could be observed and the experiment is therefore inconclusive.

[1] Schultz-Sellack [Pogg. Ann., 143, 444 (1871)] explains the action of varnishes, which he himself noticed, by the assumption that coating the particles of silver iodide prevents them from separating and occupying a larger space.

"If the clouding is really due to iodine being set free from the film by light, there will either be no clouding or a much weaker one if *the setting-free of iodine is made more difficult by the presence of iodine vapor in the surrounding air.* Two identical silver iodide plates were obtained by cutting a single plate in two, and were placed in two identical vessels of plate glass, one filled with pure air while the other also contained iodine vapor supplied by some solid iodine in the bottom of the vessel. The two plates were exposed to the electric arc under the same conditions of time and distance, but the result was not what was expected. The plate in the iodine vapor clouded surprisingly quickly and about ten times as long an exposure was necessary to produce the same result with the plate standing in air. This experiment proves conclusively that *the clouding of the silver iodide is not due to the loss of iodine.*

"Since the collodion layer does not prevent the clouding by checking the transfer of iodine from the film to the air, the only way in which it can act is by keeping the air from the silver iodide. If this view is the right one, the change of the silver iodide must depend on the nature of the gas in which the plate stands during the exposure.

"A careful investigation along this line confirmed this idea completely. Pairs of practically identical silver iodide plates were exposed under as nearly as possible the same conditions except that one plate stood in pure air and the other in an atmosphere of *hydrogen* or *nitrogen.* It proved sufficient to drive the air out of the vessel for an hour, the opening of the vessel being turned down or up, depending on whether the gas was lighter or heavier than air. The plates standing in air clouded fairly rapidly but the changes were so slow and so slight in the other gases, especially when they had been carefully purified, that *silver iodide may be considered as completely unchangeable when exposed in absolutely pure gases of this type.*

"Since air helps the clouding and since this is not due to the nitrogen it must be due to the oxygen. As a matter of

fact a silver iodide plate clouded a little, though not much, faster in an *oxygen atmosphere* than did the check plate in air. We must therefore conclude *that air increases the rate of clouding and that oxygen is the important factor.*

"The most probable assumption is that illuminated silver iodide takes up oxygen forming an *oxygen compound.* The clouding might then be due to the tensions resulting from an increase of volume when oxygen was taken up. If these tensions exceeded the tensile strength of the salt the whole film would be broken to pieces. The film must become thicker when exposed to light. On examining in sodium light the interference fringes formed by a thin film of air enclosed between the surface of the silver iodide and a superimposed glass plate, a displacement of the fringes at the edges of the illuminated portion showed that the silver iodide film did become thicker when exposed to light. It is not permissible, however, to deduce the existence of an oxygen compound from this swelling of the film, for any other change which disintegrated the silver iodide would necessarily make the film thicker.

"The possible oxygen compounds are silver oxide, silver iodate, and silver oxy-iodides. The first two substances do not form the substance of the clouded film because both Ag_2O and $AgIO_3$ are readily soluble in ammonia. They could therefore be extracted from the illuminated silver iodide by means of this solvent[1] and could then be precipitated by hydrochloric acid as silver chloride. Repeated experiments failed to show the formation of silver chloride even though the concentrated ammonia solution, in which the plates lay for several hours, was filtered, and evaporated to dryness, hydrochloric acid being added a drop at a time to the aqueous solution of the residue. Even under the microscope no precipitation of silver chloride could be seen, though it was easy to recognize the characteristic crystalline form of the silver iodide which had been dissolved by the ammonia and

[1] [Barium chloride is quite soluble in water but it can only be washed out of barium sulphate with difficulty.—W. D. B.]

which precipitated on evaporation. Also, a silver iodide plate which had been clouded by light was not changed by standing for hours in ammonia.

"We shall have a definite proof that the cloudy substance is not an oxygen compound if we can cause the clouding when oxygen is *completely excluded*, as for instance in an atmosphere of hydrogen in presence of any substance, such as iodine, which helps on the clouding. Hydrogen was passed for an hour and a half from above into a bell jar made out of plate-glass plates cemented together and was drawn off at the bottom. After that, some platinum lying in the bottom of the bell jar and covered with iodine, was heated electrically until the iodine vaporized readily. A silver iodide plate hanging in the bell jar was then exposed to the light of the arc. The plate clouded very rapidly, much more rapidly than a check plate exposed alongside in the open air.

"If the material of the clouded film is not an oxygen compound, the only other hypothesis seems to be that it is *pure silver iodide*. This conclusion is supported by the following experiments. It is known that silver iodide is dimorphous and that above 146° it changes from the hexagonal to the regular system. This is characterized by a change in color, for the regular modification is much more brilliantly yellow than the hexagonal one. If a silver iodide plate is clouded markedly in one spot by an exposure to light and is then heated, preferably under a Lehmann heating microscope with low magnification, there soon appears above the flame a dark yellow-colored spot which gradually spreads. The yellow color appears just as soon, and the spot expands just as fast, on the clouded portions as on the clear portions, a proof that the former contains normal silver iodide. The length of the exposure is entirely without effect. Even after an exposure of hours, when the film undergoes no further change in light, and one may assume that all possible changes have taken place, the yellow color can still be observed very clearly if the plate is heated.

"A silver iodide plate was clouded very much in spots by

light and was laid with the film side on the smooth bottom of a glass vessel containing distilled water. If a sodium thiosulphate or a potassium cyanide solution be added carefully, there is a gradual dissolving of the silver iodide and a slow moving forward of the solution. It is noticeable that the cloudy parts dissolve just as readily and as completely as the clear parts and that the line of solvent action in one part is a continuation of the corresponding line in the other part.

"From these experiments we may conclude that *the clouded film is formed of pure, mechanically disintegrated, silver iodide* and that oxygen plays the part of a catalytic agent promoting the formation of an intermediate state. The processes taking place when silver iodide is exposed to light are to be conceived of in the following manner.

"According to Arrhenius, illuminated silver iodide is dissociated and therefore the stability of the compound is decreased. A complete decomposition will take place only in presence of some substance which can combine with silver or with iodine. It is known that Vogel[1] explained the sensitizing action of some solutions on silver iodide collodion by the assumption that iodine reacted with these solutions and was thus to a certain extent absorbed and removed from the silver iodide. In the present case, silver must form some such compound as Ag_2O with the oxygen of the air and silver iodide is therefore decomposed more readily in presence of oxygen. This silver oxide, being instable in the light, must break down and the silver thus formed will react with the iodine from the previous decomposition to form silver iodide again, when the same process goes on anew:

$$2AgI + O = Ag_2O + 2I = 2AgI + O = \text{etc.}$$

There must therefore be a continuous rearrangement of the atoms whereby a disintegration and clouding of the whole film takes place.

"It is of course unimportant whether Ag_2O is formed or some other substance which decomposes readily in the

[1] H. W. Vogel: Handbuch der Photographie, 1, 193 (1890).

light. The essential thing in the explanation is that the oxygen, by forming a compound, causes the complete decomposition of the already dissociated silver iodide and that there is at once a regeneration of the original system, a formation anew of the silver iodide from which we started.

"It is obvious that under these circumstances *iodine must be more effective than oxygen.* On account of the greater affinity of iodine for silver, a compound which can be decomposed by oxygen will be decomposed much more readily by iodine.[1] For the same reason it is clear why the clouding takes place more readily the greater the excess of iodine in the plate exposed in air.

"It ought also to be mentioned here that a silver iodide plate which was originally clear and which stood in a space filled with iodine vapor, gradually became cloudy even in the dark, the time for the change varying from hours to days, depending on the temperature, and therefore on the partial pressure of the iodine. The explanation just given applies also to this case provided we supplement it by the assumption that, in presence of an excess of iodine, silver iodide is also somewhat dissociated in the dark.

"If a sufficient illumination be given to a pure silver iodide plate, a distinct image can be developed physically, but the time of exposure has to be enormously greater than that for an ordinary daguerreotype plate with a silver backing. This possibility of development does not necessarily depend on a chemical change in the exposed film. Since the mercury and the silver of the physical developers precipitate especially readily on rough spots, the possibility of developing these exposed silver iodide plates may well be the result of the roughening of the surface at the exposed portions due to the disintegration of the film.

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[1] The experiment does not succeed with chlorine and bromine because the plate becomes cloudy very quickly in these gases even in the dark. [The author appears to overlook the fact that chlorine and bromine set free iodine from silver iodide. The argument in regard to oxygen and iodine sounds like reasoning in a circle. No equation is written for the decomposition of silver iodide by iodine, though this should have been done. W. D. B.]

Action of light upon silver iodide backed with silver

"We have now to investigate what reactions take place when we expose a normal daguerreotype plate, in other words a silver iodide film backed with silver. Here there will also be a dissociation of the illuminated silver iodide, and the complete decomposition into silver and iodine will perhaps take place more readily because the silver of the backing may take up the iodine. One would therefore expect that the silver plate would gradually become iodized and the silver iodide be reduced to sub-iodide.

"This *iodizing of the silver* actually takes place and can be shown in a very pretty way. A silver film is precipitated chemically on glass. The film is made so thin that it is fairly transparent. This film is iodized according to Wiener's directions so that a wedge-shaped silver iodide film is formed. When seen from the glass side, the plate appears as a fairly uniform mirror with a bright metallic lustre. When looked at from the film side, very beautiful interference colors are to be seen on the thin silver iodide film. If one exposes part of the plate with the film side to the electric light, while the rest of the plate is kept shaded, the following things can soon be seen. The shaded portion is unchanged; but, where the light has fallen on the plate, the metallic lustre has disappeared from the glass side. This is more marked the thinner the silver film, and is therefore seen most clearly at the edges of the plate. Instead of the original metallic lustre, there are now unmistakable, and sometimes quite bright, interference colors. The front side of the plate is also changed where it has been exposed to light. Here the interference colors became paler and paler until they disappeared, when the film seemed to be covered with a substance having an intense metallic lustre. We thus have the surprising result of a reversal of the original system. The unexposed film had a metallic lustre on the glass side and interference colors on the air side while the exposed film showed interference

colors on the glass side and metallic lustre on the air side.[1]

"By this experiment we overthrow the assumption that a homogeneous film might be formed consisting of a silver sub-iodide. Such a film must obviously look the same from either side. The matter is however not so simple as all that. One might then picture to himself that iodine, as the more rapidly moving ion, would move fastest from the place where the intensity of light was greatest, so that silver would remain behind. On the assumption that the iodine when set free will be absorbed elsewhere, the silver must pile up where the intensity of the light is the greatest. In other words, the silver moves against the light or, more properly speaking, the iodine moves with the light. How far such factors may come in, will be discussed later. The explanation does not hold for this case because the same changes take place even when the plate is lighted from the glass side, though of course they require more time because of the loss in intensity when the light passes through the sheet of silver.

"Since the results of a preceding section pointed to an effect at the surface of the silver iodide, it seemed wise to make experiments on a film partially covered with collodion, shellac, or something of that sort. It turned out that *changes in the covered portions took place very much more slowly* than in the parts of the plate exposed to the air. The back of the plate lost its metallic lustre much less and the front kept its interference colors for a much longer time.

"The changes in the film could also be modified by pressing down a glass lens. In the places under pressure there was no decrease in the metallic lustre of the silver sheet and only a slight change in color could be detected on the front side. On the other hand, when the glass lens was removed and a new exposure to light was made, it appeared

[1] Schultz-Sellack [Pogg. Ann., 143, 446 (1871)] exposed a daguerreotype having a very thin silver backing and noticed a decrease in the metallic lustre on the back of the silver plate, corresponding to the illuminated portions, thus showing that the silver had become thinner. On the other hand he did not notice the appearance of interference colors on the back nor of a metallic lustre on the front.

that the changes took place much more slowly than on a portion which had never been under pressure. The rather considerable pressure of 100–150 atmospheres had slowed up the whole process very considerably.

"The effect of the protecting covering of collodion, etc., is evidently not because of any prevention of the transfer of iodine into the air for if no such transfer takes place with pure silver iodide plates, it is quite impossible that it should occur in this case where the iodine is so much more easily held back. There is therefore only one conclusion possible, that *the oxygen of the air has a positive influence in promoting the changes.*

"In order to strengthen this view, it seems natural to attempt to expose the silver iodide film backed with silver in an atmosphere of hydrogen, etc. Numerous experiments along this line gave no very clear result. It is true that in two cases it was clear that equal exposure affected the plate in hydrogen distinctly less than the plate in air. In the other cases no difference could be detected, not even when the hydrogen was purified by passing through an alkaline solution of pyrogallol. It is however possible that small amounts of oxygen were still present, which were perhaps enough to cause the changes of the plate in the light.

"If it therefore seems permissible to ascribe to the oxygen of the air a direct and helpful part in the changes undergone by a silver iodide film backed with silver, the strong metallic lustre makes the normal silver oxide, Ag_2O, the only oxide to be considered. Its presence could not be shown by treating with ammonia and subsequent addition of hydrochloric acid to the solution. The appearance of the plate was not changed in the slightest by the action of different reducing agents or by a gentle heating of the plate. We are therefore forced to conclude that *in this case also oxygen acts only catalytically.*

"The process taking place during the illumination must run in something like the following way: The cohesion of the silver iodide is broken up by the light, and the compound decomposes in the presence of oxygen, into silver oxide. The iodine which is set free diffuses through to the back of

the silver iodide film where it meets and iodizes the metallic silver, thus disappearing from the stage. Since there is no oxygen at the back of the silver iodide film there can be a dissociation but no complete decomposition of the silver iodide there. The silver oxide, formed on the front of the film, is soon decomposed into silver and oxygen. According to the way of looking at things, the illuminated film consists of silver in front (in contact with air) and of silver iodide[1] at the back (in contact with glass).

"The silver precipitated by light is by no means a coherent metallic silver, as the material from the plate was made by iodizing. The difference can be detected by the somewhat brownish appearance and the less brilliant lustre. The illuminated film also does not conduct the electric current, although the resistance of the plate was not very high before the exposure to light. But this silver is converted very easily by iodine vapor into silver iodide and the silver iodide film thus obtained, although slightly clouded, behaves in every other respect like one made from freshly-precipitated silver. The silver is probably more or less nearly *molecular*, which is not surprising in view of the way it was prepared."

"Of course it must not be concealed that the theory which has been outlined does not account for all the phenomena which may be observed when we expose plates consisting partly of silver and partly of silver iodide. There are evidently other factors whose effects I have not been able to explain satisfactorily. Yet I wish to discuss one point which is evidently of the utmost importance, namely the *difference in the intensity of the light inside the film.*

"It has previously been mentioned that silver iodide has an enormous absorbing power for violet light, in other

[1] L. Moser [Pogg. Ann., 56, 191 (1842)] states that he has exposed a yellow-iodized silver plate for two months by daylight, has rubbed it off with dry cotton so as to remove the upper layer of the "blackened" silver iodide, and has then found the film to be as sensitive as it was in the beginning. He rubbed off the surface again and exposed the plate to an intense light, doing this eight times and always finding a sensitive silver iodide distributed uniformly over the plate.

words for the light which is photographically the most effective. Since the exposure was always made with white light, the violet light was the important factor in the phenomena described. It was also pointed out that when there was a great difference in the intensity of the light inside the film, there must be a tendency for the iodine to diffuse to the places where the intensity of the light was least. If the effective violet light is absorbed very much in passing through the film, the iodine will collect chiefly at the point where the light leaves the film, *i. e.*, the iodine will move with the light and will leave the silver on the front of the film.

"Such an action of the iodine can actually be observed experimentally. A carefully-washed silver iodide, precipitated from a silver nitrate solution by potassium iodide, was placed between two glass plates into which platinum mirrors had been burned. The whole was placed in a muffle furnace, heated until the silver iodide was liquid, and then cooled slowly. The plates did not fit exactly one on the other but were staggered a bit so that it was possible to connect the two platinum plates to the two leads of a galvanometer. On exposure to light there was a throw of the galvanometer needle which always indicated a positive current flowing through the electrolyte (AgI) in a direction against that of the light, regardless of which plate was exposed. If one let the light fall first on one and then on the other of the plates the throw of the needle was first one way and then the other provided the connections were not changed. The reversal of the current proved that the light gave rise to a new electromotive force and that the current was not due merely to a decrease in the resistance of the cell in consequence of the dissociation of the silver iodide.[1] If one takes into account that the transport of electricity is due chiefly to the iodine ion (the migration velocity of the silver ion being relatively

[1] The electromotive force in this experiment was about 0.05 volt. The white light of the arc was made parallel by means of a lens and was filtered through a vessel containing an ammoniacal copper oxide solution.

small) it follows that in this experiment *the iodine always moves with the light.*

"On silver iodide plates backed with silver, similar phenomena can also be observed. This will only succeed however if one neutralizes the effect of the medium in contact with the sensitive film, the air, by embedding both sides of the iodized silver film in the same medium, gelatine for instance. Half of a wedge-shaped, iodized, silver plate was exposed to light until the interference colors appeared on the glass side. The limiting line of illumination was perpendicular to the interference fringes. The film was removed from the glass by means of gelatine, then covered with gelatine, and cut in two along the edge of silver iodide double wedge. One-half was now exposed from what had been before the glass side and the other from what had been the air side. When the light passed through the film from the silver iodide to the silver, there was a perceptible change during the exposure, so that silver could be recognized by its metallic lustre on the front of the film and silver could be recognized at the back of the plate by the interference colors. On the other hand when the light passed from the silver to the silver iodide, this state remained, there being the least change on the half that had previously been exposed, and a little more on the half which had not previously been exposed. On this latter there was a slight disappearance of the metallic lustre and a slight paling of the interference colors, but these changes were insignificant and not to be compared with those when the light passed in the other direction. In general, then, the experiment confirmed the view that iodine tends to move in the same direction as the light.

"In the normal daguerreotype plate, which receives the light from the front, it is evident that the decreasing intensity of light as it passes through the iodide film will cause a precipitation at the surface just where it also occurs under the influence of the oxygen of the air. These two causes thus work together. If the daguerreotype plate were exposed from the glass side, the two forces would work against

each other and it would depend on circumstances which would be the more effective. As a matter of fact one gets more complex results in any such arrangement.

"The iodine, set free by the joint action of light and the oxygen of the air, diffuses through the film of silver iodide and reacts with the silver backing, converting it into silver iodide. This migration of the iodine can evidently take place without difficulty when violet light is the exciting agent because this is absorbed by silver iodide so completely that no stationary waves are formed. In this case the intensity of the light decreases continuously from the surface between the air and the silver iodide to the surface between the silver iodide and the silver. As the iodine passes from the front to the back it is moving always toward a place where the intensity of the light is less. The situation is somewhat less simple when blue light is used, because then stationary waves are formed and it is not easy to see how the iodine, on its way to the rear, can pass from a node into a loop of the stationary light wave, since it must then be moving against an increasing pressure of iodine. If we take into account the fact, established by the experiment with the galvanometer, that iodine moves rapidly from the places where the intensity of light is greatest, we can get around this difficulty in a simple way. As soon as blue light falls upon the plate and as soon as the stationary waves are formed, iodine begins to pass from the loops to the nodes, thus decreasing the pressure of iodine in the former and increasing it in the latter until the differences are smoothed out more or less, and so it becomes possible for the iodine to move to the rear.

"Finally I must consider the possibility of iodine in a *discharged state* passing through the silver iodide film. One may imagine some such state of things as this. The oxygen at the front takes the charge from the iodine so as to form silver oxide with the charged silver left behind. The iodine dissolves in the silver iodide and diffuses through it to the back. Such a dissolving and diffusing of the iodine through

the silver iodide is what we have to assume in the ordinary iodizing of a silver plate.

"Whether one makes the assumption of charged or of uncharged iodine, in any case *electrical charges* must appear throughout the process in different portions of the plate and there must be electrostatic forces acting; for in order to have iodine ions reach the surface of the silver and to cause an iodizing, that means, according to Nernst's views, that the moving iodine ions bind a number of the silver ions which maintain the equilibrium between the electrolytic solution pressure of the metal and the electrostatic forces. Therefore positively charged silver ions must go into solution and the metal must remain charged negatively. When we have spoken of oxygen taking the charge from the iodine, that was merely a short expression for a series of more or less complicated processes connected with movements of ions and therefore with changes of charges. In fact, neither the decomposition of silver oxide into unchanged silver and oxygen nor the formation of silver iodide from unchanged silver and iodine is intelligible without the appearance of electrical charges. If these have not been observed in the reactions in question, that is probably because the potential differences are not very large because they are continually eliminated by local currents, just as the potential difference, which determines the equilibrium between zinc and sulphuric acid, is not maintained when the zinc is impure.

"From what has been said, it appears that a knowledge of the electrical charges involved is essential to a complete understanding of the reactions which occur when a daguerreotype plate is exposed to light. External conditions forced me to bring my work to a temporary close and to leave the solving of the still unsettled problems to a later time. I felt that this was the more permissible because the final results of this investigation and their application to the theory of the daguerreotype process are not affected thereby. In fact, a clearing up of the dark points would probably give us a deeper insight into the details of the reaction and might

bring out a connection between these phenomena and Hallwachs' phenomenon of photo-electric excitation."

"In a paper read before the French Academy about two years ago Demole[1] discusses the effect of washing the plate after exposure in a bath containing a weak oxidizing agent and then developing by candle light instead of in the dark.

"Three facts have long been known: 1. That a photographic plate, treated with potassium bichromate, washed and dried, and exposed behind a negative, may be developed in full daylight, a reproduced negative being obtained. 2. Prolonged exposure to light affects the latent image in such a way that there is reversal on development. 3. That the film, when exposed in the presence of oxidizing bodies, is particularly liable to reversal.

"I propose to consider the action of weak oxidizing agents on the latent image—not such as are used for its destruction, but those which form a new combination with the latent image which permits of distinctions being made as to the constitution of the latter.

"When a plate wh ch has received an exposure is placed for a few minutes in a one percent solution of potassium ferricyanide, and is rinsed and developed in hydroquinone, potash and sulphite, two facts are noticed. The first is that the plate may have been very greatly over-exposed without the developer being any the quicker or the result being any the worse. The oxidizing agent plays the part of a regulator of the exposure. The second fact is that if one develops by the unscreened light of a candle the result obtained will be negative instead of positive, as it would have been by red light. Reversal thus takes place, even after a very short exposure, but a stronger image is obtained after a more lengthy exposure.

"These facts, it would seem, should be distinguished from those known as solarization, although this phenomena is always the characteristic of a prolonged exposure.

[1] Brit. Jour. Photography, **54**, 346 (1907).

"The regulation of the time of exposure by means of an oxidizing agent can be applied to certain bromide papers—for example, to the "Orthobrome" paper of the firm of Gevaert, of Antwerp. The only necessary precaution is to add five percent of glacial acetic acid to the oxidizing solution.

"If the exposure is prolonged above a certain limit the image undergoes a second reversal, the inverse of the first. Thus, exposing a Lumière "blue label" plate behind a negative at 50 cm from an arc lamp a good positive copy is obtained in one second when development is done in red light. With increased exposure the plate is oxidized, and on development in white light the result of from one second to 170 seconds' exposure is reversed, *i. e.*, a negative. From 180 seconds' exposure, development gives at first a positive, which, little by little, with increasing exposure, becomes negative. From seven minutes' exposure a positive still shows, and does not distinctly alter but the high-lights are not clear. From fourteen minutes' exposure the positive is persistent, and one has, in a way, realized the much-sought-after problem of development in daylight.

"It is assumed that the latent photographic image consists of a silver sub-bromide, Ag_2Br, resulting from the decomposing effect of light in the presence of a bromine absorbent, such as gelatine; the sub-bromide being a very unstable body, will be readily oxidized to an oxy-bromide of the formula Ag—O—Br, according to the hypothetical equation:

$$4Ag_2Br + 4H_2O + 3O_2 = 4AgOBr + 4AgOH + 2H_2O.$$

"This hypothetical oxy-bromide of silver, oxidized with difficulty by the developer alone, is more easily reduced by the combined action of developer and light, but is less quickly reduced than the surrounding silver bromide which has not been acted upon. Hence it is that the latent image being stable, and its immediate surroundings not so, the image is reversed. It should be said, in conclusion, that the hypothesis which takes this reaction into account is based

on the existence of silver sub-bromide as a constituent of the latent image, an assumption yet to be proved."

The editor of the *British Journal of Photography* comments upon this paper as follows:

"It is quite possible that there may be some hidden principle or value in M. Demole's experiments, but at first sight the facts as cited by him are not consistent with the ordinary phases of solarization.

"Dealing first with his statement of an over-exposed plate with ferricyanide, it would be as well to point out that this is not a newly observed fact. It has been pointed out by Sterry (1899), Lüppo-Cramer (1901), Schaum (1903) and Eder (1902), that any oxidizing agent destroys the solarized silver bromide image and leaves behind that on the normal silver bromide. This being the case it is obvious that the developer will not be any the quicker nor the result any the worse. Can it be said, therefore, that the ferricyanide is 'a regulator of the exposure?' The second observation (that a negative is obtained instead of a positive when developing is effected by candle-light instead of red light) merely confirms a fact that has long been known, and which we personally have applied before now for obtaining a positive or reversed negative, and that is that as soon as development has proceeded to some extent by red light a flash of white light will reverse the image.

"Exactly how these facts differ from solarization is not clear. That the procedure can be applied to bromide paper is a natural corollary, and, speaking from personal experience the slower the sensitive salts the more successful this method of reversal.

"Dealing with the prolongation of exposure, one should bear in mind that Janssen pointed out that there were successive stages with prolonged exposure, and that to obtain a second negative image from a primary negative required an increase in exposure of 100,000 times the normal. This statement has also been confirmed by Eder, who, using a Chapman-Jones sensitometer plate, finds that (assuming that

a vigorous half-tone in a negative required an exposure of one to two Hefner candle-meter-seconds) a distinct reversed positive required an exposure of 300,000 H.c.m.s. Thus the exposures given by M. Demole of fourteen minutes are much below this limit. True, he says, that with this exposure and subsequent treatment with ferricyanide 'one has, in a way, realized the much-sought-after problem of development in daylight;' but, by the well-known principle of utilizing an oxidizing agent he would have destroyed his solarized image, or, to put it in other words, have rendered it incapable of being developed. The result must be then a positive, because the bromide of silver that is left in a developable condition is the reverse of the negative image.

"There is also one other action which M. Demole recognizes in the case of bromide paper, but not in the case of the plate, and that is the action of the ferricyanide on the gelatine itself. This it is well known is a hardening action, and it might have to be taken into consideration. Further than that, one must also assume the possibility of some interaction between so powerful an oxidizer as ferricyanide and the hypothetical silver sub-bromide, which, as Dr. Homolka suggests, can be easily split into Ag + AgBr. This being the case, one may have, as pointed out by Dr. Sedlaczek in his work on toning bromides with ferricyanides, and by Mr. Douglas Carnegie in his article on 'The Chemistry of the Sulphide Toning Process' ('B.J.A.,' p. 907, p. 676), a complex of silver ferrocyanide which would be impermeable to a developer."

The question of the effect due to illumination of the plates during development has been studied systematically by Nipher[1] in a series of papers read before the Academy of Sciences of St. Louis and published in its Transactions.

The following quotation is from a paper[2] entitled "On Certain Properties of Light-struck Photographic Plates."

"The results to be given in this paper were obtained with

[1] I am greatly indebted to Professor Nipher for reprints of these papers.

[2] Nipher: Trans Acad. Sci. St. Louis, 10, 151 (1900).

a Töpler-Holtz machine having one 24-inch plate, and with no condenser attached to its terminals. The spark-length mentioned in the paper is the distance between the discharge knobs of the machine.

"A parallel circuit consisting of ball-tipped brass rods about six feet in length led to the insulated stool upon which the photographic plate is placed for electrical exposure. A brass plate a foot square was placed on the top of an insulated stool, and formed one plate of a condenser. Upon this a much larger glass plate is placed, upon which rests the photographic plate. All of the results were obtained with the Cramer 'lightning' plate. Some metallic object like a medal is placed upon the sensitive film, and forms the other plate of the condenser. A rod about a foot in length, having knobs, stands vertically over the medal. The knobs of the secondary or parallel circuit are separated from the plates of the condenser and from the machine terminals, by small spark gaps which may be varied. Such changes appear to materially affect the behavior of the machine and the details of the picture produced. The rods are all sleeved by glass tubing, and are then held by laboratory clamp stands. This arrangement for electrographing is well known although the photographic plate has heretofore been protected from the light.

"The method which has been found most convenient for manipulation is to first expose the plates to the light of an ordinary room for from one to nine days. A longer interval has not been tried, but some of the best results were obtained from the last of a box of plates which were all exposed at the same time, and which were not all used until nine days had elapsed. This method of treatment is advantageous because it is difficult to prevent light from the discharge from striking the plate during the electrical exposure, and a great over-exposure renders the plate more manageable in the subsequent treatment. It darkens much more slowly in the developing bath than when slightly light-struck.

"The plate is put in position with the medal resting upon

it. The capacity described gives a rather rapid sequence of small sparks, which may be made 15 cm in length. At each discharge between the knobs of the machine, a discharge occurs on the film around and under the medal. This exposure may be from four to ten minutes. A much longer exposure reverses the picture and gives a positive. The exposure should be in a darkened room, and the light from the spark should be kept from the plate by a screen. Light falling on the plate while the electrical action is taking place, counteracts the electrical action in a very remarkable way. This may be shown by partly closing the blinds of a window ten or fifteen feet away, forming thus a vertical slit a foot in width. The other blinds are to be wholly closed. A book set up so as to shade half of the plate yields results such as are shown in Fig. 1.[1] This print is of course a positive from the original negative.

"It is therefore evident that the time of exposure depends somewhat on the diffuse illumination in the room. A very dark room is not necessary.

"It is also found that if the plate be exposed to light for a day or more after the electrical exposure, a similar counteracting effect is produced. In this way the picture may even be reversed and develop as a positive.

"In developing the picture a cool and rather weak hydrochinone developer leaves nothing to be desired. The room should not be too dark during this operation. The best conditions are to be found in an ordinary dark room, lighted by a single incandescent lamp. The light should be five or six feet away, and any tendency to fog is remedied by taking the plate nearer to the lamp. If already fogged, a plate may thus be cleared up in a very remarkable way. If the plate is too near the light during the whole time, there is a loss of detail. By allowing the developing to begin four or five feet from the lamp, moving it up as necessity arises to within two or three inches, and with a cool and weak developer,

[1] [The figures referred to in the text are not reproduced in this article.]

the picture may be developed for an hour if desired. During this time the details are coming out with continually increasing sharpness.

"When the spark length is less than 12 or 13 mm, no disruptive and luminous sparks are seen on the plate. There is a violet corona around the medal. The pictures given by the positive pole show radial discharges, bounded by a dark, band, like a halo. For short spark lengths of 5 or 6 mm the halo is close around the medal, and it increases in radius as the spark length increases. With a spark length of about 16 mm, a dark halo appears distinctly on the plate before developing. This has been seen only a few times. Thus far it has not been found possible to save it. It washes out in the developer. It begins to fade and an inner one, apparently midway between it and the medal, begins to appear. The outer halo has disappeared, before the inner one has fully developed. When the developing is arrested at an earlier stage, the outer ring is lost in the fixing bath.

"The shape of the dark halo conforms to the general shape of the body. In some cases, where the disruptive effects of exceptionally strong character have passed, their tracks are shown on the negative. These tracks are in all cases distinctly broader and darker where they cross the dark halo, than elsewhere." . . .

"Fig. 10 is a reproduction of a portion of a negative showing ball tracks magnified about one hundred diameters. While these tracks were being traced, disruptive sparks were passing continually over the plate, and the tracks appeared somewhat obscured when viewed with the unaided eye. A pocket lens showed well-defined tracks, and in the enlarged photograph the blurred effect has entirely disappeared.

"This picture has been reversed twice, and shows the tracks in black as they appear on the original negative.

"The fact that greatly over-exposed plates may be developed in the light, was suggested by the fact that in exposure to light during the taking of an electrograph, the electrical action was annulled. Finally when a plate which at first

promised well began to fog in the dark room, the light of an incandescent lamp was turned on, and the plate at once cleared in a most remarkable way.

"This again suggested the idea of developing X-ray pictures in the light. This has also been done with very satisfactory results. Light-struck plates were used for this purpose, which had been exposed for a day to the diffuse light of the laboratory. Singularly enough these pictures were negatives when they were enclosed in black paper during the X-ray treatment, and they were positives if they were exposed to the light while the X-ray was acting.

"The advantage of being able to study an X-ray picture during the operation of the developing is sometimes very great. The operation may then be pushed until the desired features have been brought out, and it may be arrested before they are obscured by over-developing.

"When the X-ray is thrown upon a plate in a camera while an ordinary picture is being taken, all exposed parts of the plate are affected alike. The action of light and of the X-ray are added. If a picture be taken of a diagram in black on white cardboard, the action of the X-ray will be shown equally on the dark and on the light parts of the image. This is made evident by shielding half of the plate from the X-ray by a screen of metal or of lead glass. There is a marked difference between this result and that found for the superposition of light and electrical action, as is shown in Fig. 1. In order that the X-ray picture of the metal fittings of the camera, and the light picture of the object in front of the lens may be superposed on the fixed plate, the diaphragm of the camera must be so set that the two pictures will develop in the same time with the same developing bath.

"The results already described suggested that in ordinary photography the exposure might be so modified that the picture might be developed in the light.

"In the first attempts that were made the object was a street scene. The exposures were from one to three and a fourth hours. The pictures developed in the light with per-

fect clearness. They are of course positives. They appear somewhat unpromising at first, while in the developing bath, and one is tempted to abandon them as failures, as indeed some of them may be, until experience is gained. The pictures obtained by these long exposures show some very interesting features. They show no trace of moving objects on the street. In some cases hundreds of people passed. In one case ten street cars were blocked for twelve minutes, in the foreground, and cars were passing at the rate of 70 to the hour. Wagons were driven to the curb to deliver goods, and people were standing on the street corners waiting for cars. In an exposure of an hour no trace of these objects could be seen on the plate when developed. The street appeared absolutely deserted. The car tracks show with distinctness. In one exposure of three hours and forty-five minutes a team and wagon stood in one position for twenty-eight minutes, and no trace of them appeared. If the exposure of the same plate is only for one second, these moving objects are all shown. Another feature of these long exposures is the entire absence of shadows. It is somewhat difficult to account for this, as it hardly seems possible that their motion is sufficiently rapid to produce this result. The sky appears absolutely uniform. Clouds which were in marked contrast in one case yield no trace upon the picture. An attempt was then made to shorten the time of exposure and still permit development in the light. This was done by subjecting the plate, while in the plate holder, to the X-ray. The plate holder was held for ten minutes, six inches from a Crookes's tube operated by a large induction coil in oil. A perfect picture of the hand could be obtained in six to eight seconds. The same plate was then exposed for two hours to a Crookes's tube operated by a large eight-plate influence machine. The plate holder was then put into the camera and exposed to a street scene for ten minutes and was then developed in the light. The result is shown in Fig. 11. For reproduction of form and shadow, this plate could hardly be excelled by a transparency made in the ordinary way.

Like the others, it shows no trace of moving objects on the street.

"It has long been known that a slight over-exposure of a plate in the camera sometimes gives a positive picture when developed in the dark room. The experience thus far described made it seem probable that such pictures might also be developed in the light. This was found to be the case. If the proper exposure is one and a half to two seconds, an exposure of a minute is sufficient. Some that have been made have not been very satisfactory. But one has been obtained which is even superior to the plate reproduced in Fig. 11. It is shown in Fig. 12. For richness of finish and for perfect modulation of light and shadow, this original plate leaves nothing to be desired. During most of the time while being developed, it was held one foot from a sixteen-candle lamp. During some of the time it was held nearer, and during some of the time it was five or six feet from the lamp.

"Figs. 11 and 12 are of course reproductions of the original positives. In these exposures the Cramer isochromatic plate was used.

"In some of these shorter exposures where people or wagons halted on the street, they are shown on the fixed plate. Where they were motionless during the whole exposure they are of course shown with perfect clearness.

"Experiment shows that a conspicuous object two feet in breadth and fifty feet from the camera if moved transversely at the rate of twenty feet per minute, during an exposure of one minute, will show on the plate as a distinct trail. With a longer exposure it is eliminated. The unit of exposure may be roughly considered as one candle-meter-second. With a fixed illumination, the exposure may be varied, by varying the time of exposure. It appears that for any exposure, there is some definite degree of illumination in the dark room, which will yield what might be called a zero plate. No picture will appear on it if lights and shadows are each uniform on the object, as in case of a diagram in black on

white cardboard. This picture will become a negative in a darker, and a positive in a lighter developing room. With an exposure of half a second a plate which will develop as a perfect negative in a proper dark room, will develop a zero plate if the room is dimly lighted. In the parlance of the photographer, it will fog. In a still brighter light it will develop as a positive. In this action there must be a time co-ordination in the action of the developer and the light of the dark room. With a given strength of developer it appears from results thus far obtained that a maximum degree of excellence will be secured with a definite degree of illumination in the dark room. The results thus far obtained with half-second exposures, are by no means satisfactory, considered as products of the photographer's art, but the pictures of street scenes are distinctly positives. If results comparable with those for longer exposures are attainable, it involves a delicate adjustment of the illumination of the dark room and strength of developer which has not so far been secured.

"With an incandescent lamp burning in the dark room, it is easy in half-second exposures to obtain a rather poor negative, by holding the bath in the shadow of an object eight or ten feet from the lamp. By holding the plate in the light, and going somewhat nearer, the same plate with the same exposure, will yield a picture which is distinctly a positive.

"With a very much over-exposed plate, it is difficult to get a room dark enough to yield a negative. With a very short exposure, it is equally difficult to get positives, and only by a very great illumination of the plate while in the developer. The condition of zero plate when only the time of exposure and the illumination of the developing room are variable, certainly cannot be very different from an inverse proportion. The experiments thus far made show also that with a long exposure, the best results can be obtained by developing the plate in the light, as a positive, while for very short exposures the best results are obtainable by developing as a negative.

"These conclusions may be modified by a variation of

the strength of the developer. The limits within which the variables may change and yield results of commercial value have not been determined with precision for positive pictures. What has been said of pictures taken in the camera, may also be said of X-ray pictures on plates not previously light-struck. If two plates are exposed in the same way to the X-ray, and one be developed in the dark and the other in the light, the former develops as a negative and the latter as a positive. Either may be converted into a zero plate by a change in the illumination of the plate while in the bath, as has been previously explained. The more careful study of these subjects is still in progress. There is ground for believing that the treatment of a plate by a slab of plaster of Paris moistened with peroxide of hydrogen, according to the method used by Russel[1] may be of value in developing X-ray pictures in the light. Work in this direction has not yet progressed sufficiently to warrant any final conclusions.

"The superposition of X-ray pictures on electrographs does not as yet reveal any effect of either agent upon the action of the other. This has been done with fresh plates and with those which had been previously light-struck. In these experiments half of the plate was shielded from the X-ray by a heavy plate of lead glass. The pictures due to the two sources were superposed, and the two effects were added where simultaneously acting. This is also in marked contrast to the action of light on the electrograph, as is shown in Fig. 1.

"The superposition of X-rays upon a plate in the developing bath while in a dark room promises interesting results, but so far this has not been done from lack of time."

From a paper entitled[2] "Positive Photography with Special Reference to Eclipse Work" I make the following quotation:

"If the object to be photographed is a landscape, consisting mainly of mid-summer foliage, and the plate be a

[1] Science, March 30, 1900, p. 491.

[2] Nipher: Trans. Acad. Sci. St. Louis, 10, 210 (1900)

fast plate, like the Crown plate of Cramer, the exposure may be made two to four minutes in length. For the first attempt the latter interval is to be preferred. The exposure may be made as much longer as may be desired. It has been successfully tried with exposures of six and eight hours.

"The plate is taken to the dark room and is best developed by the light of a strong lamp. If the exposure has been not over two minutes, the best result will be obtained by placing the bath between two strong lamps. Two Argand or Rochester burners with porcelain shades in contact or nearly so, with the bath in a position of strongest illumination between and below the shades, is an admirable arrangement. The bath should be cool at the start, and it should be in ice-cold water during the development. The bath being rather weak, the development will go on very slowly.

"Various developers have been tried. Pyro has given very poor results, although the same bath would yield brilliant negatives in the dark room. By far the best results have been reached by the use of Cramer's hydrochinon developer, the formula for which may be found in every box of Cramer plates. This formula is:

	Ounces	Grams
Water	25	1000
Sulphite of soda	3	126
Hydrochinon	1/2	21
Solution No. 2		
Water	25	1000
Carbonate of soda	6	252

"The two solutions are to be mixed in equal parts, when used, and are to be diluted to from one-third to one-fifth strength. A few drops of 10 percent solution of bromide will give brilliancy to the plate, but will not improve definition of details. The bromide may be left out.

"In transferring the plate from the holder to the de-

veloping bath, it would seem to be somewhat better to turn the lamps down until the liquid covers the plate, but the light should then be turned on at once. When lamplight is used this precaution is not very important. In fact the writer is inclined to say that such precaution is not then necessary. If the exposure has been too small, either from insufficient light on the object, or from insufficient time, such an exposure in the light room is a decided advantage. It carries the plate farther from the zero condition, and materially improves the picture. The same result may be secured by turning the camera upon the sky after the usual exposure to the object has been made, and before the shutter has been closed. This sky-exposure may be for half a minute with a No. 8 stop, but should not exceed this. The following experiment seems to indicate that this sky exposure should be after rather than before the exposure to the object.

"A white paper was pasted on a somewhat larger card of dead black. It was placed against a brick wall in sunlight, and with a cloudless sky. After a minute of exposure to the plate in the camera, the black card was quickly shifted laterally by a distance slightly greater than its width. This was repeated ten times in an exposure of ten minutes. On developing, the first of the ten exposures was somewhat more distinct than those which followed, but between the others no difference could be detected. The last minute of the ten was as effective as the second. But when the experiment is terminated at the end of the first minute, the image is very indistinct. It is evident that the subsequent exposure during the nine minutes served to make more distinct the image of the card made during the first minute. And since the plate seems to be somewhat more sensitive at first than it is later in the exposure, it is better to utilize this part of the exposure in securing details of the object, rather than in fogging the plate beyond the zero conditions. This difference of sensitiveness is not very marked. It is difficult to see any difference in the first three and the last three minutes of a six-minute exposure. This may be shown in an interesting

way by the following experiment: The experimenter should preferably be dressed in light-colored clothing, and should train the camera on a grass-covered hill, which will serve as a background. Any other dark background will of course answer the purpose. After snapping open the shutter, walk to a point about 100 feet distant, the camera having been focused for that distance, and stand motionless for two or three minutes. Then step sidewise four or five feet and stand for an equal time. Then walk back and close the shutter. The two figures will seem practically alike if the sunlight has not changed, and the darker background will not appreciably show through them. The plate will show no trace of the motions, and the figures will be as clear and distinct as in a good negative.

"Of course the same thing can be done in the ordinary negative process by so arranging the conditions that the time of exposure is sufficiently lengthened.

"In order to make the positive photography as useful as possible, it is necessary to find a developer which will bring out a clear positive with as small an exposure as possible. It seems certain that it must differ from any developer used in ordinary photography. The method of restraining an over-exposed negative is known, in order that it may be developed as a negative. If we consider this plate as an under-exposed positive, how shall it be pushed along over the zero condition, and developed as a positive? That answer may be given in part. It must be developed in the light. A poor negative may be developed in a lighted room, and a poor positive may be developed in a dark room. These are not the conditions which yield the best results.

"The writer had great expectations of the developer used by Waterhouse for producing positives in the dark room with ordinary exposures. The formula for this developer, as given in various works on photography, is:

		Parts
A.	Eikonogen	5
	Sulphite of soda	10
	Water	100
B.	Carbonate of soda	4
	Water	100
C.	Phenyl-thiocarbamide	1
	Water	2000

"For developing take of A 1, of B 2, of C 1 and of a 10 percent solution of potassium bromide 1. If the contrasts are too strong, a few drops of ammonia may be added.

"This developer is said to produce a positive in the dark room, with ordinary exposure. It was hoped that this urea salt either in the Waterhouse developer, or in some other, and with development in the light, might shorten the camera time very greatly.

"When the exposure is normal for a negative, and the plate is developed in the dark room with this developer, it is found that a yellow to orange coloration appears in the shadows. If there are contrasts on the object, the high-lights look as they do in an ordinary negative. The roof of a building and the sides lighted by direct sunlight appear as in an ordinary negative. Light and dark strips of slate will appear reversed. The sky is dark. The sides in shadow are of a yellow or orange color, sometimes almost red, and appear as positives. If the exposure is increased somewhat either by an increase in time, by stronger illumination of the object, or by using a larger stop opening, the coloration disappears, and the whole picture is seen to be a negative. A still greater exposure being made, the picture approaches, and finally becomes a zero result. Nothing develops on the plate. With a still longer exposure the picture is reversed, and a real positive develops. This picture can be developed in the light. This is not the case with the Waterhouse pictures. They look like positives, as any negative may be made to look like a positive, but they should be called pseudo-positives. They are not due to a real reversal. They are moreover

somewhat disappointing in appearance. It is only too evident that this Waterhouse process does not seem to be a very promising field for application to eclipse photography, although it presents some very interesting illustrations of different forms of silver.

"The most promising field for investigation at present consists in the application of some transforming process to the film, after it comes from the camera, and before the picture is developed. Various oxidizing agents have been tried with different degrees of success. The most satisfactory of these oxidizing solutions is a mixture of nitric acid and potassium bichromate in rather dilute solution. There is no trouble in getting very satisfactory results with four minutes of exposure and a No. 8 stop. It seems very probable that by varying the proportions of this transforming solution, and perhaps varying the oxidizing agents themselves, such exposures as are now given in the negative process, may yield good positives. The field open for experimentation along these lines is very wide. The degree of illumination while in the transforming solution and the time interval for the transforming process are involved. The desirability of perfecting these processes at the earliest possible moment, leads the writer to urge those who have had wider experience in photography to lend a hand in this work. If fine details can be secured in a positive with a camera exposure such as is now required for a negative, then certainly there is a great reason to hope that by exposing a plate during the whole time of totality in the long eclipses which will shortly take place, we may hope to secure better results than the present methods can give. In positive photography there can be no over-exposure. In negative photography, over-exposure is an approach to a zero condition. In positive photography the zero condition has been passed."

The most important[1] of the series is one entitled "The Relation of Direct to Reversed Photographic Pictures. This I

[1] Nipher: Trans. Acad. Sci. St. Louis, 11, 51 (1901).

quote in full, omitting all the illustrations except the one diagram.

"In former papers in these Transactions[1] the author has given a partial exposition of the results of developing photographic pictures in the light. These results were reached in the course of a long series of experiments, in which the films were acted upon by electrical discharge. It was found that the most rapid plates might be exposed to daylight for a week, and that contact electrographs of coins might then be produced in a well-known way. It was also found that these pictures might be developed in the light, and that for exposures to electrical action with a Holtz machine for several minutes, these pictures were negatives. The parts of the film most exposed to electrical action came out dark when developed either in the dark room or in the light, but those developed in the light were clearer and gave less trouble from fog. The significance of this was not then fully realized, and there remain yet many points to be cleared up by further study. Since that time specially treated plates have yielded negatives in the light from ordinary camera exposures and they showed a marked improvement when the light was turned on. But the method is not as yet under sufficient control so that the results can be obtained except at rare intervals.

"The results given in the former paper seem to have been misunderstood by many, who have apparently supposed that the author was not aware of the fact that photographic positives had long been known as a result of developing greatly over-exposed plates. This was expressly stated in the first paper referred to, and it was clearly pointed out that development in the light was the feature to which attention was invited.

"In the present paper the conditions which yield direct and reversed pictures will be given. The work has been restricted to Cramer's "crown" plate, and the developer used was hydrochinon. The plates were all exposed in a printing

[1] Trans., Vol. X., Nos. 6 and 9.

frame either to the light of an incandescent lamp or to daylight. The pictures were all printed from the same lantern slide, or positive, so that the direct pictures are all negatives, and the reversed are all positives.[1] The over-exposed negative and the under-exposed positive require the same kind of treatment. A restrainer must be used, whose function is to keep away the fog. The fog is incidental to an approach to a zero condition in which the plate will be blank. The restrainer does not change the character of the picture as regards positive or negative. It is not necessary to use it for what are called normal exposures, when negatives are developed in the dark room, nor for normal exposures when positives are developed in the light. The amount of restrainer used must increase as the zero condition is approached. The amount needed may be as great as a twelfth of the entire bath in ten percent solution of potassium bromide, and this may be supplemented by the addition of from two to five drops of saturated solution of sodium hyposulphite. When the picture to be developed is a landscape with modulated lights and shadows, any exposure from normal to more than ten million times over-exposed may be developed in the dark room. As the zero condition is reached, the strongest highlights will reverse, and the other parts of the picture will locally reverse as greater exposures are given, but without complete loss of detail. There will be incongruities in light and shadow, and each local detail will have at a certain exposure, a minimum of distinctness. A picture in which the shadows are alike, and likewise the lights, will develop a blank at the zero condition. This would be the case if a punched stencil in cardboard were printed upon a sensitive plate.

"The zero condition does not seem to be affected by varying the strength of the bath. If the plate be first placed for a minute in a normal bath, it may then be transferred to and

[1] This method of exposure was adopted in order to secure known conditions of illumination. For some of the longer exposures, a 300-candle Packard incandescent lamp was used, and was found very satisfactory. This lamp was kindly furnished by the manufacturers.

developed in a bath as weak as one-tenth the normal strength. The positive and negative features are then the same as when developed in the normal bath. If the plate is first placed in the weak bath, the solution does not wet the film uniformly, and the plate appears as if it had been attacked by a painter's brush while the gelatine was soft.

"There is little need to lose any valuable landscape exposure entirely if the plate is from the first treated as an over-exposed plate, until its condition is known.

"The plate from which the printing was done is reproduced in Fig. 1, Plate 2.[1] When exposed for one second at a distance of a meter from a 12-candle lamp a normal negative results from development without restrainer. When the exposure has been increased to 53 minutes 20 seconds or 3200 seconds, the strong light across the walk to the left of the picture begins to reverse, and appear white as positive. The original slide does not quite cover the sensitive plate below. On a narrow strip along the left edge of the picture, the plate is fully exposed to the light. This part also begins to reverse at the same time as the high-light mentioned. In diffuse daylight ten feet from a south window when the sky is as clear as it usually becomes in St. Louis, during the winter, the picture will begin to reverse with 16 seconds of exposure. This time varies somewhat with variations in illumination and only rough approximations are possible. This daylight is therefore actinically about 200 times as active as one lamp-meter, which required 3200 seconds to produce the same result. As the exposure increases, other parts of the picture reverse. The light on the monk's lap will finally reverse, and appear white, while the part below in shadow will also appear white, because it is still a negative.

"Such a result is shown in Fig. 11, Plate 7. The penumbra which separates light and shadow appears then darker than either the lighter or the darker areas adjoining. Never-

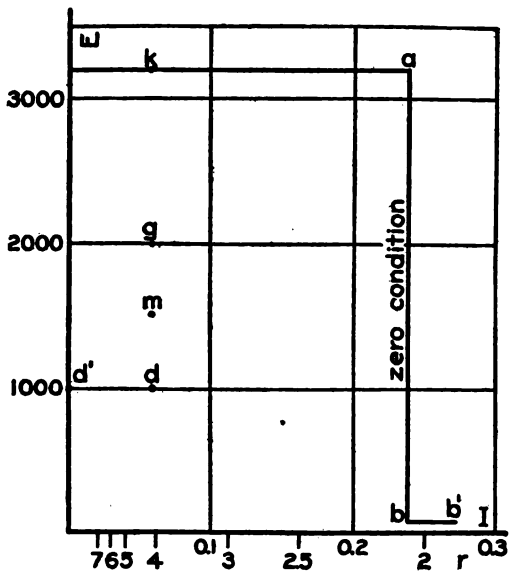
[1] The picture was not formed symmetrically on the plate, and the transparent border is lacking on one side of the picture. The picture was obtained by an artist friend in Southern California.

theless the whole figure of the monk shown in the foreground is sharply differentiated from the background. The dense foliage to the right of the picture is still a negative, while the entire left half of the picture has reversed. When the exposure time has increased to about ten minutes of daylight, or 120,000 lamp-meter-seconds, the last detail of the picture has just reversed or is about to reverse. This part is the deep shadow among the foliage in the right of the picture. In Fig. 12, Plate 7, the picture is all reversed, excepting a small area of the darkest foliage.

"When the exposure has been increased to two hours, a sharply defined positive, yielding a good print, is yet obtained. It is, however, somewhat dense, and prints slowly. The picture from this exposure is reproduced in Fig. 13, Plate 8. The exposure for this plate is equivalent to $7200 \times 200 = 1{,}440{,}000$ lamp-meter-seconds, or over 16 lamp-meter-days.

"When instead of developing the exposed plate in the dark room, it is developed at a distance r = seven meters below a 16-candle lamp, the plane of the filament being horizontal, a similar series of pictures is obtained as the exposure time increases. The picture begins to reverse exactly as in the dark room, when the exposure in lamp-meter-seconds is 3200. All exposures less than this give negatives, of surprising merit. The positive or reversed pictures having a greater exposure than 3200 cannot be distinguished from those made in the dark room. In the diagram representing the conditions of exposure and development, the co-ordinates are exposure E, in lamp-meter-seconds, and illumination, I, in lamp-meters, of the developing bath. The value of I is $\frac{1}{2}$, where r is the distance of the bath from the 16-candle lamp. The value I is laid off on the horizontal axis of the diagram, and the numbers representing distances r, ranging between 2 and 7 meters, are indicated along the axis I at places on the scale which those distances determine. For example where $r = 2$ meters, the value of I in lamp-meters

is $\frac{1}{2^2} = 0.25$. The vertical axis E, where I = 0, corresponds to $r = \infty$. This vertical axis therefore represents increasing exposures in the dark room.



"For all values of I less than $\frac{1}{(2.05)^2} = 0.238$ the picture begins to reverse when the exposure time is 3200 seconds, exactly as has been described for dark room development. This value of I is a critical value. When the developing plate has this illumination, a zero plate is obtained for all exposures between 53 and 3200 lamp-meter-seconds. The zero line which for smaller values of I was the horizontal line E*a*, of the diagram, drops straight down from *a* to *b*. As this line is approached from the negative side, the picture becomes more and more obscure, and on reaching it the plate is blank, with the exception of a few faint isolated features here and there, some of which appear to be positive and some negative. If I is made slightly greater than this critical value, the picture wholly reverses and becomes positive as soon as E exceeds 53 seconds. For slightly smaller values the picture is a poor negative. The line *b b'* is a sharp line of separation between positive and negative results, and no

mongrel pictures are produced in the transition. The line *b b'* is not horizontal. When the picture is developed at a distance $r = 1$ meter, for which $I = 1$, faint positive pictures are obtained with an exposure of 25 lamp-meter-seconds. Thus far it has been found impossible to develop any negatives in this light. The zero line evidently approaches the axis I for illumination greater than the critical value $I = 0.238$. For daylight development the picture evidently starts from a positive condition, just as for small values of I it starts from a negative condition. When the plate is illumined with the critical illumination there is probably some condition of chemical instability which would render the plate photographically sensitive to feeble influences which under other circumstances might have no discernible effect. This might apply to electrical oscillations. This critical condition has been very carefully studied photographically, and plates have been produced along the entire range represented by the line *a b*, both on the negative and on the positive side.

"The area on the diagram representing the conditions where good photographic positives can be produced has not yet been adequately explored. An attempt was made to form an exhibit of developed plates which would show by inspection the results obtainable with various exposures E, and illuminations I of the plate while developing. The plates were laid upon a large table at points determined by the co-ordinates E and I. In order to properly represent dark-room work, the scale of E should be at least one meter for one lamp-meter-second. Ordinary dark-room work with ordinary over-exposures would then require a table a few meters in length. The time of exposure which will yield good positives has, however, been found so large that the plan proved impracticable. Fig. 15, Plate 9, is a reproduction of a picture which had an exposure of 16 hours to diffuse daylight. The value of E in the diagram was about $16 \times 3600 \times 200 = 11{,}520{,}000$ lamp-meter-seconds. This would be equivalent to a continuous exposure of four months to a 16-candle lamp at a distance of 1 meter. The position of this plate on the

exhibition table would be at a distance E = 11,520 kilometers or about 6,900 miles from the axis I. The plate was developed in a glass tray in diffuse daylight with reflected light thrown up through the bottom of the tray. The value of I was therefore over 200, which is about 800 times the value that could be represented in the diagram. With these long exposures the best results have been obtained by reflecting light through the bottom of a glass tray, while the plate is being developed. If this cannot be done, the plate should be lifted out of the liquid at intervals, and the bottom should be exposed to the light. Fig. 16, Plate 9, shows a trace of two ribs in the bottom of the developing tray which cut off part of the light.

"These long exposures show wonderful detail in the darker shadows. They show with clearness details that are barely distinguishable in the original plate from which the printing was done. Referring to the plates,

"Fig. 1 is a positive, from which all the printing was done.

"Fig. 2 is a negative, printed from 1, with an exposure of one lamp-meter-second, E = 1, and developed in the dark room. These conditions are represented by a point in the diagram which is practically at the origin O.

"Fig. 3 is a negative having an exposure E = 1000, and developed in the dark room. The point in the diagram is marked *d'*.

"Fig. 4 is a negative having an exposure 1000, and developed at a distance *r* = 4 meters below 16-candle lamp. The illumination is I = 0.0625. The point in the diagram thus determined is marked *d*.

"Fig. 5 is a negative having an exposure E = 1500, and developed exactly like No. 4. The point in the diagram is marked *m*.

"Fig. 6 is also a negative, having an exposure E = 3200, and developed under the same conditions as Figs. 4 and 5. This picture has just begun to reverse. The light on the walk just beyond the pan, has begun to turn white. The picture is rather dense, but the details are sharp. The bright strip

around the picture has also become lighter. Point *k* in the diagram represents the conditions.

"Fig. 7. The plate here reproduced has had the same exposure as the last, but it was developed 1 meter below three 16-candle lamps. Hence I = 3. The diagram does not extend beyond the value I = 0.25.

"Fig. 8. This plate had an exposure E = 3200 like the last, but the value of I = 100.

"Fig. 9. The exposure was E = 24000 and the plate was developed in daylight where I = 200. The plate is wholly reversed.

"Fig. 10. Exposure E = 36,000, I = 200. This picture is a clear positive, and was developed without any restrainer.

"Fig. 11. This plate had an exposure 60000, and was developed 2.25 meters below a 16-candle lamp. The value of I = 0.197. This is somewhat less than the critical value of I, represented by the line *a b* in the diagram. The picture has only in part reversed, although the plate last described, with an exposure only a little more than half as much, was fully reversed, because of the larger value of I.

"Fig. 12. This plate had an exposure E = 120,000.

"The value of I = 0.0625. The only part of the plate which is still negative is a small area in the dense foliage in shadow, on the right of the picture.

"Fig. 13. Exposure E = 1,440,000. I = O.

"This picture is completely reversed.

"Fig. 14. This plate had the same exposure as the last, but was developed in daylight where I = 200.

"Fig. 15. Exposure 5,000,000. I = 200.

"The details in the dense shadows are admirably shown in this picture. The exposure was seven hours to diffuse daylight in front of an inclined skylight about ten feet square. The exposure was to a northern sky.

"Fig. 16. This exposure was made like the last one, but lasted for sixteen hours on two days. The plate was developed in the same light, with a mirror reflecting light upward upon the under side of the plate.

"Fig. 17. This picture is from the negative shown in Fig. 2, Plate 2. It is a reproduction of a print from that negative, which was made by ordinary methods. It is to be compared with Fig. 18, made from the same original as Fig. 16, which is from an exposure 11,500,000 times as great.

"A number of good pictures have been developed in direct sunlight, but they have been lost or destroyed, and it has since been found difficult to produce as good ones as were formerly made. There is strong evidence that there is a discontinuity in the conditions of sunlight development like that shown by the zero line at the critical illumination. One difficulty in the study of this subject, is the extreme variability of sunlight. The actinic value of sunlight is also enormous compared with the standard illumination used in this work. An exposure of about a quarter of a second is greater than an exposure of 120,000 seconds at a distance of 1 meter from a 16-candle lamp. The developing of good pictures in direct sunlight is therefore in an uncertain condition as yet, and is receiving further study.

"If the plan of laying the developed plates down upon a table at points determined by E and I, had proved practicable, it would have been possible to draw on the diagram, lines passing through points where the plates have an equal excellence. These lines might be considered to be contour lines surrounding the summit of a surface. This summit, representing the maximum of excellence of negatives would be on the vertical axis, E, and very close to the origin. It would correspond to normal conditions for dark-room work. The surface would sink to a minimum along the zero line shown in the diagram, and would then rise again in the immense field representing the conditions under which positives may be developed. The conditions of maximum excellence for positives are yet unknown, but the best pictures yet obtained, which seem to be as near perfect as could be wished, had exposures of two and a half minutes in strong diffuse light just outside of direct sunlight at a south window. This

illumination was probably about 400, on the scale used in this paper. The pictures were developed at the same point.

"In the pictures here represented the plates have all received uniform treatment. No shading of highlights have been done. In the etching during the half-tone reproduction all parts of the plate have been treated alike.

"In reproducing Fig. 6 it was found that on account of a muddy background effect in those parts of the plate which were about to reverse, the original did not submit itself readily to the half-tone process. Details which could be clearly seen could not be satisfactorily reproduced. The plate was therefore re-photographed by ordinary means, and from this plate a print was made which has been reproduced in half-tone.

"This plate having an exposure of 3200, marks the beginning of reversal. All exposures greater than this lie above the horizontal zero line. The picture does not wholly reverse until the exposure has reached 120,000. This broad belt of mongrel effects extends along the whole length of the horizontal zero line, from dark-room conditions to critical illumination. The upper limit of this belt will of course vary with different plates, depending upon the density of the plate in the deepest shadows.

"So soon as the plate is developed in a light stronger than the critical value, no mongrel effects appear, and the exposure time for a plate yielding zero drops at once to 0.016 of 3200. In these stronger illuminations is therefore a field of promise for positive photography with short exposures. It may perhaps require a modification of the developer, the plate emulsion or both, in order to secure the best attainable results."

In Part III I shall take up Wood's experiments on the Clayden effect, and on the reversals as obtained by Trowbridge I shall also include an account of Trivelli's conclusions and of the reasons for them. We shall then be in a position to consider the subject as a whole and to see in how far one hypothesis will account for all the phenomena.

Cornell University

FERRIC NITRATES AT 25° C[1]

BY F. K. CAMERON AND W. O. ROBINSON

Schönbein[2] was the first to publish descriptions of the ferric nitrates. No analyses were given, though several basic salts were described. Ordway[3] prepared $Fe_2O_3.3N_2O_5.18H_2O$ by adding nitric acid, specific gravity 1.42, to a solution of ferric nitrate of a density of 1.27 and cooling to 15° C. He succeeded in preparing solutions carrying as high as 24 equivalents of ferric oxide to one equivalent of nitric acid. He found that these solutions were of a colloidal character. Hausmann[4] prepared the dodecahydrate of the normal nitrates by crystallization from a solution containing an excess of nitric acid. By boiling solutions of the above named crystalline salt he obtained the following basic nitrates: $8Fe_2O_3.2N_2O_5.3H_2O$; $36Fe_2O_3.N_2O_5.48H_2O$; $8Fe_2O_3.N_2O_5.12H_2O$.

Scheurer-Kastner[5] confirmed Ordway's work by preparing the normal nitrate with 18 molecules of water. By boiling normal ferric nitrate solutions products were obtained which he identified as the following supposed compounds: $2Fe_2O_3.N_2O_5.H_2O$; $2Fe_2O_3.N_2O_5.2H_2O$; $4Fe_2O_3.N_2O_5.3H_2O$. Ditte[6] describes a ferric nitrate of the composition $Fe_2O_3.3N_2O_5.6H_2O$, formed by the action of very concentrated nitric acid on the ordinary crystalline salt. Wilderstein,[7] Heldt,[8] Berthelot,[9] and others have studied ferric nitrates, confirming the composition of the 18 and 12 hydrates of ferric nitrate.

It will be seen that the formulas given for the basic ferric nitrates are confusing, and the fact that the ratios of

[1] Published by permission of the Secretary of Agriculture.
[2] Pogg. Ann., **9**, 141 (1836).
[3] Am. Jour. Sci. (2), **9**, 30 (1850).
[4] Liebig's Ann., **89**, 109 (1854).
[5] Ann. Chim. Phys. (3), **55**, 330 (1859).
[6] Comptes rendus, **89**, 641 (1879).
[7] Jour. prakt. Chem., **84**, 243 (1861).
[8] Ibid., **90**, 257 (1863).
[9] Ann. Chim. Phys. (4), **30**, 167 (1873).

ferric oxide to water are much the same, regardless of the basicity of the mass, tends to throw discredit upon the definite composition formulas hitherto assigned to these basic bodies.

To test this point, ferric nitrate solutions of varying concentrations were shaken up with freshly precipitated ferric hydroxide at a constant temperature (25° C.) for four

TABLE I

Composition of solutions of ferric nitrate and respective solid phases with adhering mother liquor at 25° C

Solution			Solid phase with adhering solution		Solid phases
Sp. gr.	Fe_2O_3 Percent	N_2O_5 Percent	Fe_2O_3 Percent	N_2O_5 Percent	
1.032	1.78	2.21	—	—	Fe_2O_3-mN_2O_5-nH_2O
1.055	2.86	4.03	26.02	5.45	"
1.079	3.99	5.61	—	—	"
1.085	4.58	7.16	29.25	7.93	"
1.127	5.79	9.00	—	—	"
1.146	6.61	10.41	28.83	9.03	"
1.177	7.22	12.31	24.02	11.11	"
1.204	8.00	13.65	—	—	"
1.264	9.70	16.60	—	—	"
1.303	10.86	19.58	23.48	13.09	"
1.368	12.48	22.70	23.96	15.26	"
1.397	13.66	26.29	25.93	16.78	"
1.435	14.62	28.13	—	—	"
1.498	15.40	29.52	—	—	"
1.496	15.22	30.5	19.60	40.3	$Fe_2O_3.3H_2O_5.18H_2O$
1.464	13.13	32.8	19.03	40.0	"
1.452	12.14	33.5	19.82	40.4	"
1.434	9.95	36.3	19.62	40.3	"
1.431	9.21	36.2	19.48	40.6	"
1.417	7.25	40.3	19.20	40.2	"
1.409	6.11	42.7	19.66	40.3	"
1.404	5.02	47.5	18.92	40.5	"
1.428	3.55	51.5	19.38	39.8	$Fe_2O_3.3N_2O_5.18H_2O$
1.450	4.51	52.0	19.64	40.3	"
1.465	4.49	55.2	19.18	41.0	"
1.407	3.93	47.2	17.50	46.6	$Fe_2O_3.4N_2O_5.18H_2O$
1.419	3.52	49.6	17.70	46.9	"

months. At the end of this time the clear solutions and the precipitates with adhering solution were analyzed. The iron was estimated in the usual gravimetric manner and the nitrogen by conversion to ammonia with aluminum, zinc, and sodium hydroxide. The acid branch of the isotherm was studied in a similar manner, but starting with ferric nitrate and various concentrations of nitric acid. The data obtained are given in Table I and plotted in Fig. 1.

From the figure it is apparent that there are no definite basic nitrates of iron formed at 25°, and the so-called salts are solid solutions of ferric oxide, nitric acid and water, for the lines joining the points representing composition of the

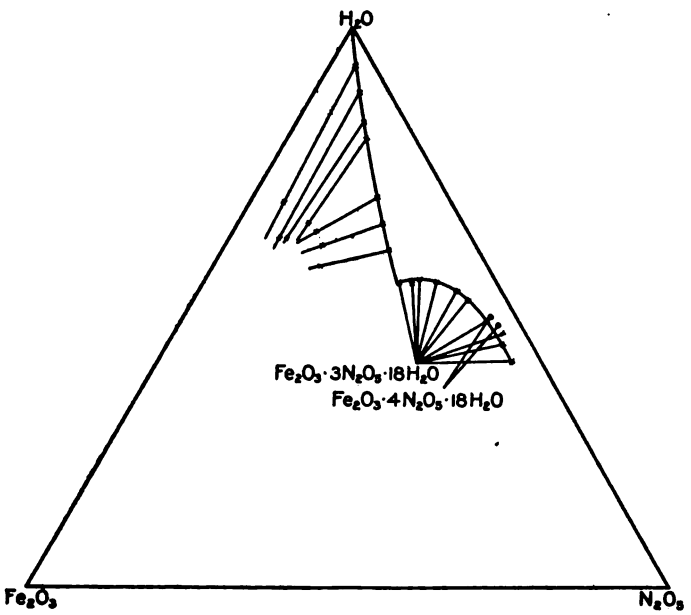


Fig. 1

liquid and its respective solid phase with adhering solution do not meet at a common point or points. When nitric acid is in excess, however, the lines do meet at a point, and this point, scaled off, corresponds to $Fe_2O_3 \cdot 3N_2O_5 \cdot 18H_2O$. Two bottles contained a crystalline salt different from the

rest in appearance. These crystals gave a colorless solution in water 1 : 100, whereas a solution of the normal 18 hydrate was yellow. The yellow dilute solution of the normal nitrate can be made colorless by the addition of two equivalents of nitric acid, which gives a solution of the same ratio of acid to base as the acid nitrate. The lines joining the points representing the composition of the liquid and solid phases with adhering solution met at a point corresponding to $Fe_2O_3.4N_2O_5.18H_2O$.

This acid nitrate, from the fact that its solubility is less than the normal nitrate, would seem to be the more stable. All the acid nitrate obtained was used in the analyses before it was realized that there would be any difficulty in again obtaining it, and for this reason solutions were not inoculated with both forms of crystals. Later attempts to obtain this acid salt have failed, the normal salt being obtained in all cases.

From the table it will be seen that the normal 18-hydrate salt possesses a somewhat higher solubility than does the new acid salt just described, though the difference is slight, considering the concentration of nitric acid. It would appear that the temperature chosen was near the transition temperature of one of these salts to the other, and very probably under these conditions the rate of transformation is slow. It is also obvious that the data for some of the points given at the higher concentrations cannot correctly represent final equilibrium conditions. But the high concentrations make the experimental and analytical work unusually difficult, and it has not been deemed worth while for the intrinsic value of the data to devote further time to the problem.

In this paper it is shown that there are no definite basic nitrates of iron formed from solution at 25°, and that the solid phase under these conditions is a solid solution of ferric oxide, nitric acid and water. The normal 18-hydrate exists in stable equilibrium in solutions containing a little more than 30 percent N_2O_5, up to a concentration of 45 percent N_2O_5, and it is usual to find it in solutions up to 55 percent

N_2O_5. In these higher concentrations of nitric acid it appears to be metastable and a new salt—$Fe_2O_3.4N_2O$—probably with 18 molecules of water of crystallization is the stable form. This latter, however, has been realized but twice.

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ELECTROLYTIC PRECIPITATION OF CUPROUS OXIDE

BY D. MILLER

One of the problems of long standing which has confronted the electrochemist is the question of making white lead electrolytically which shall be able to compete in quality with the product made by the "Dutch Method." Practically all the electrolytic white leads which have been made are failures apparently for two reasons. They are too transparent and absorb too much oil. This may be attributed to the fact that electrolytic white lead is crystalline while the other is amorphous. The problem then becomes simply a question of determining under what conditions we shall be able to obtain electrolytically a white lead which shall be dense and amorphous.

Before taking up the above problem, it was thought that a study of the characteristics of electrolytic precipitates, obtained under varying conditions, might, in the future, help in its solution. For the sake of convenience in the laboratory, it was decided to work with cuprous oxide instead of white lead, because it was known that the color varies markedly with the conditions of precipitation. With this end in view, a hot solution of sodium chloride was electrolyzed between copper electrodes and the cuprous oxide thus formed examined under the microscope, the color as well as the size of the particles being noted. The effect of varying the temperature, current density, and concentration of the electrolyte was studied as well as the effect of adding a little gelatin to the solution.

Variation of Temperature

The precipitates we obtained at various temperatures between 60° and 100° showed marked differences. The color and size of the particles varied directly with the temperature, the darker and larger aggregates being formed at the higher temperatures. In order to be certain that the pre-

cipitates contained no cuprous hydroxide, samples were taken in which the electrolysis had taken place and boiled for not less than fifteen minutes. This operation produced no change either in the size or the color of the particles. Since cuprous oxide is known to precipitate from solutions at 100°, it was supposed that cuprous hydroxide would dehydrate at the same temperature. Since no color change was observed, it was assumed for a while that the precipitates were all cuprous oxide and that the color changes were not connected with any change of composition. Subsequent analyses by Mr. Gillett showed that this was not the case and that the precipitates have compositions varying continuously from that corresponding to cuprous hydroxide to that corresponding to cuprous oxide. The yellower the precipitate, the more nearly the analysis will correspond to the formula for cuprous hydroxide while the intense red precipitates approximate fairly closely to the formula for cuprous oxide.

This introduces an annoying complication because the change in the size of the particles very probably depends on the change in composition as well as the changes in the other factors. Fortunately, it was found that it was comparatively easy to duplicate the colors with a very fair degree of accuracy. In order to avoid circumlocutions, the word cuprous oxide will be used in this paper to mean precipitates obtained at 60° or upwards, regardless of the actual composition of the precipitates.

These results of the temperature variations are tabulated in Tables I and III.

Variation of Current Density

An increase in the current density causes the particles to become smaller and lighter in color. This is what would necessarily be expected since small particles are always produced when a precipitation is rapid and larger ones when it is slower. At a high current density, the cuprous oxide is precipitated rapidly and consequently the particles are

small. A 10% solution of NaCl was used in this experiment.

TABLE I

Color changes

Current density Amp/dm²	100°	90°	80°	70°	60°
1.125	Dark red	→	→	→	Light red
2.25	↓	→	→	→	↓
3.75		→	→	→	
6.0		→	→	→	
7.5	Light red	→	→	→	Light orange

The arrows indicate that the colors grade in the direction in which they point between the shades named above. No appreciable color changes took place when solutions, precipitated at 60° or 70°, were boiled for a short time.

TABLE II

Sizes of particles in thousandths of a millimeter

Amp/dm²	100°	90°	80°	70°	60°
1.125	6.4	6.4	4.8	4.0	3.2
2.25	3.2	3.2	3.0	3.0	3.0
3.75	3.0	3.0	2.8	2.6	2.4
6.0	2.8	2.6	2.4	2.0	1.6
7.5	2.6	2.4	2.0	2.0	1.2

These measurements were made with a microscope in the usual way, a micrometer eye-piece, which had been previously calibrated, being used and the crystals floated in glycerine. They represent the average diameter of the single particles. While they may not mean much as absolute measurements, still they do show that the particles are smaller at the lower temperatures and higher current densities than at the higher temperatures and lower current densities respectively. From these two tables, the following conclusions can be drawn. The color varies with the size of the crystals the darker color being present when the particles

are large. Since the samples were not analyzed when prepared, it is impossible to distinguish accurately between the change in color due to change in chemical composition and that due to change in size of particle. The change in composition is, however, the more important factor.

Variation of Concentration

The current density was held constant at 3.75 amperes per square decimeter while the concentration of the electrolyte was varied. In the samples obtained, we find that neither the color differences nor the variation in size of the particles are as marked as in the preceding case. The figures given in Table IV are practically worthless as regards any difference in the size of the particles. If it were possible to get greater magnification, one might find that at the higher concentrations, the particles were smaller, as the data to a certain extent seem to indicate. The objective used in making the measurements in these tables was 1/6″. As regards changes in color, it is easy to detect, that at the higher concentrations the precipitates are lighter in color. This, presumably, is due to a slight increase in the solubility of the cuprous oxide with increasing concentration of sodium chloride.

TABLE III

Color differences

Concentration Percent	100°	90°	80°	70°	60°
5	Brick-red	→	→	→	Orange
10	↓	→	→	→	↓
15	↓	→	→	→	↓
20	↓	→	→	→	↓
Saturated	Light brick-red	→	→	→	Orange-red

Here again the arrows indicate that the colors grade in the directions in which the arrows point between the shades named above.

TABLE IV

Sizes of particles in thousandths of a millimeter

Concentration Percent	100°	90°	80°	70°	60°
5	3.4	3.2	3.0	2.5	2.0
10	3.0	3.0	3.0	2.4	2.0
15	3.2	3.2	2.6	2.4	2.0
20	3.0	3.0	2.4	2.4	2.0
Saturated	3.4	3.4	3.2	2.4	1.6

The above measurements represent the average diameter of the single particles.

Addition of Gelatine

The addition of gelatine to the electrolyte caused the cuprous oxide to be precipitated in an amorphous form. One-tenth of a gram of gelatine was added to each beaker containing about 300 cubic centimeters of a 10% NaCl solution. The current density used was 3.75 amperes per square decimeter. The colors of the precipitate varied from a brownish red, obtained at 100° to a yellow formed at 60°. With larger amounts of gelatine, the precipitate assumes a greenish-yellow tint, even at 100°. The sizes of the particles were as follows.

Sizes of particles in thousandths of a millimeter

100°	90°	80°	70°	60°
3.2	2.4	2.0	1.6	1.2

The temperatures as given in this article are only approximate values, and the caption 100° merely means that the solution was heated to boiling.

The conclusions to be drawn from this work are as follows:

1. The color of the cuprous oxide depends on the composition and size of the particles, the color being darker the larger the particles.

2. The particles are larger, the higher the temperature and the slower the precipitation. The general rules of precipitation, therefore, hold whether the substance is precipitated chemically or electrolytically.

This work was suggested by Professor Bancroft and was carried out under his supervision.

Cornell University.

ACTINIC INFLUENCE ON ELECTROCHEMICAL ACTION

BY L. RAY FERGUSON

The title of this paper is a sub-head in an article on "Actinic Chemistry" published by Robert Hunt.[1] The experiments there described are discussed more fully in Hunt's book[2] from which the following quotation is taken:

"From two sets of experiments, on the electrochemical action of the solar rays, I draw these conclusions:

1st. That electro-metallic precipitation is prevented by the influence of the sun's rays.

2nd. That light is not the retarding agent, but that the exercise of electrical force is negatived by the direct influence of actinism.

"I placed in a test-tube a strong solution of nitrate of silver; in another tube, this being closed at one end with a thin piece of bladder, I placed a solution of iodide of potassium; which was supported in the solution of nitrate of silver, by being fixed in a cork, and a piece of platina wire was carried from one solution into the other. An arrangement of this kind was kept in the dark; iodine was liberated in the inner tube, and a crystalline arrangement of metallic silver was formed around the platina wire in the outer one. A similar arrangement was placed in the sunshine. Iodine was liberated in the inner tube, but no silver was deposited.

"Having exposed the above solution to the sunshine of July during a long day, the tube was placed in a dark cupboard, but the actinic influence which had been exerted on the solution of silver had produced a permanent change in its condition; after several days, no trace of any metallic deposit could be detected, but the whole of the iodine again entered into combination, whereas this was not the case in the unexposed glasses.

"In the inner tube I placed a solution of silver, and in

[1] Jour. Chem. Soc., 2, 311 (1845).

[2] Researches on Light, 290 (1854).

the outer one, the hydriodate of potash. One arrangement was kept in the dark, the other was exposed to good sunshine. In both instances the liberated iodine gave an intense yellow to the solution, and in both cases the quantity of metallic silver deposited was precisely the same.

"This yellow fluid being analyzed by the prism, was found to obstruct all the rays above the green, while it permitted the permeation of the yellow and orange rays in great quantity and power. It is, therefore, evident that the luminous rays of the solar spectrum have no power in retarding the electro-chemical action.

"The following experiment gives a pleasing illustration of the excitation of electric currents by solar agency, and their opposition to ordinary chemical action.

"Precipitate with any iodide, silver, from its nitrate in solution, and expose the vessel containing it, liquid and all, to sunshine; the exposed surfaces of the iodide will blacken: remove the vessel into the dark, and, after a few hours, all the blackness will have disappeared. We may thus continually restore and remove the blackness at pleasure. If we wash and then well dry the precipitate, it blackens with difficulty, and if kept quite dry, it continues dark; but moisten it, and the yellow is restored after a little time. In a watch-glass, or any capsule, place a little solution of silver; in another, some solution of any iodine salt; connect the two with a filament of cotton, and make up an electric circuit with a piece of platina wire: expose this little arrangement to the light, and it will be seen, in a very short time, that iodine is liberated in one vessel, and the yellow iodide of silver formed in the other, which blackens as quickly as it is produced.

"Place a similar arrangement in the dark; iodine is slowly liberated. No iodide of silver is formed, but around the wire a beautiful crystallization of metallic silver. Seal a piece of platina wire into two small glass tubes; these, when filled, the one with the iodide of potassium in solution, and the other with a solution of the nitrate of silver, reverse

into two watch-glasses, containing the same solutions, the glasses being connected with a piece of cotton. An exposure during a few hours to daylight will occasion the solution of the iodine salt in the tube to become quite brown with liberated iodine: a small portion of the iodide of silver will form along the cotton, and at the end dipping in the salt of silver. During the night, the liquid will become again colorless and transparent, and the dark salt along the cotton will resume its native yellow hue."

These results seemed so surprising that it was determined to verify them as a preliminary to explaining them. Hunt had apparently set up a cell

$$Pt \mid KI \mid AgNO_3 \mid Pt$$

and had found that iodine was set free both in the light and in the dark while silver was precipitated only when the solutions were in the dark. The appearance of silver iodide, in the watch-glass experiment, is undoubtedly the result of diffusion. In this latter experiment the resistance of the circuit is very high and the rate of electrical transference would be low in comparison with the rate of diffusion.

In my first experiment a porous cup was boiled in a potassium nitrate solution and allowed to cool in it. Inside the cup there was then placed a normal solution of potassium iodide and this cup was stood in a beaker containing normal silver nitrate solution. A piece of platinum wire dipped 1 cm into the potassium iodide solution and a strip of pure silver dipped 2 cm into the silver nitrate solution. The potential difference was measured with a high resistance voltmeter. The potential difference of about 0.3 volt did not change perceptibly when the cell was brought from the dark side into bright sunlight.

On short circuit the voltage of course dropped practically to zero. A current of 25 milliamperes passed through the cell and the iodine descended in a stream from the anode. There was a visible deposition of silver on the silver cathode.

After standing over night, crystals of metallic silver were seen in the pores of the porous cup.

Several experiments were made with other forms of apparatus but all with the same result. Metallic silver was deposited in a crystalline mass at the cathode although the couple was standing in the sun. No difference in voltmeter reading could be observed when the couple was transferred from the shadow to the sunlight or back.

In one arrangement the apparatus consisted of two glass tubes into which platinum wires were sealed. The diaphragm, if one may call it so, was a cotton thread previously washed in water. The resistance of this cell was much greater than that of the one with the porous cup and the difference of potential, as measured with the voltmeter, was only about 0.04 volt.

Other concentrations were tried without success. It appears therefore that Hunt has omitted some essential fact in his description of the experiments. This investigation was suggested by Professor Bancroft and has been carried out under his supervision.

Cornell University.

NEW BOOKS

Commercial Organic Analysis. *A Treatise on the Properties, Modes of Assaying, and Proximate Analytical Examination of the Various Organic Chemicals and Products Employed in the Arts, Manufactures, Medicine, Etc. By Alfred H. Allen. Third Edition, rewritten and revised. Volume II, Part III. Acid Derivatives of Phenols, Aromatic Acids, Resins, and Essential Oils. Revised by the Author and Arnold Rowsby Tankard. 15 × 23 cm; pp. xii + 547. Philadelphia: P. Blakiston's Son & Co., 1907. Price: $5.00 net.*—In the preface of this volume Mr. Tankard states: "The compilation of this volume was commenced as long ago as 1898 by its author, but owing to ill health the work made only slow progress. Mr. Allen's untimely death at a comparatively early age was deeply regretted by all chemists, and especially by workers in the domain of Applied Chemistry. His recognized great ability and his untiring energy secured for this treatise a unique position among the standard works on chemical analysis. After his lamented death in 1904, I undertook the completion of the volume—a task carried out in ready obedience to a special and last request of the author, who realized that he himself could not see the final completion of his work." Mr. Tankard has done his work in a most creditable manner and has produced a volume which compares very favorably with the earlier ones of this very valuable treatise.

The first part of the book takes up the acid derivatives of the phenols and the aromatic acids in much greater detail than in the second edition of the work. The rest of this volume is devoted to the resins and essential oils and this part of the book has been expanded from about twenty-five pages in the first edition to four hundred in the present.

Each subject is preceded by a theoretical discussion of the properties of the substances on which the analytical methods are based and tables are given summarizing the characteristic properties of related substances, which may be useful in identifying them. As a reference book of laboratory methods for analyzing the various organic substances considered in this volume it is simply invaluable for the technical chemist and even the scientific chemist will find here information of value to him in his work on these compounds. The book is well printed and bound and is furnished with a very complete index. Like most books, however, it contains some mistakes, most of which seem to be due to bad proof-reading. On page 5 "aseptol" is described as ortho-phenol-sulphonic acid, while according to J. Obermiller (Ber., 40, 3623, and 41, 696) it is mostly the para acid and contains very little of the ortho product. The statement on page 9 that "Diiodo-para-phenolsulphonic acid is prepared commercially in the free state by treating diiodobenzene with fuming sulphuric acid" is certainly wrong and is contradicted by the further statement appearing in the foot-note on the same page that, "in preparing the di-iodo acid, a certain amount of mono-iodo-phenol sulphonic acid is produced."

On page 21, sodium benzoate is dismissed with the brief statement that it "receives extensive application in America in the preservation of articles of food," and nothing is said regarding its harmfulness. Perhaps in view of the controversy over this matter, this is wise.

In speaking of Kolbe's synthesis of salicylic acid from sodium phenolate and carbon dioxide no mention is made of the latest and probably more correct view of the mechanism of this reaction (Ber., **38**, 1377).

In the statement on page 129 that "phthalic acid is prepared by oxidation of naphthalene by chromic acid mixture (according to Luddens, J. S. C. I., 1891, X, 758) notwithstanding the general impression that *other* compounds are destroyed by this reagent." *Other* is plainly a misprint for *ortho*, but the whole statement is wrong for practically all the phthalic acid is now made by oxidizing naphthalene with concentrated sulphuric acid in the presence of a small amount of mercuric sulphate. Under this head too the technically important dichlor- and tetrachlor-phthalic acids should at least be mentioned.

On pages 131 and 132 the formula for phenol-phthalein is wrong, though it is correctly given at the bottom of 132. Quinol-phthalein is spoken of as if it were identical with quinizarin on page 131 and all the formulas in the table on page 132 are wrong. The formulas for gallein and coerulein on page 139 are incorrect and several of the statements made regarding these substances are not true (see Amer. Chem. J., **26**, 97). On page 239 in the first foot-note the statement is made that, "Herzig makes an addition of 8 percent of *acetic acid* to the hydriodic acid." Fortunately the reference to Herzig's article is correctly given and if the user of this volume is careful enough to look the matter up he will find that Herzig really adds from 6 to 8 volume percent of *acetic anhydride*. On page 358 it is stated that "By boiling with alcoholic potash, anethol undergoes a molecular rearrangement with conversion into the isomeric body methyl-chavicol" and the reader is referred to page 357, where he will find the statement that methyl-chavicol is transformed into anethol by boiling with alcoholic potash. The first statement, of course, is incorrect and should be stricken out. These mistakes and omissions are not very serious, however, and do not detract from the very great value of the book to the working chemist.

W. R. Orndorff.

First Principles of Chemical Theory. *By C. H. Mathewson. First edition. 15 × 23 cm; pp. v + 123. New York: John Wiley & Sons. London: Chapman & Hall, 1908.*—In the preface the author says that "this small volume has been prepared for the use of the first-year students at the Sheffield Scientific School, as reference text in connection with a short course of lectures on Chemical Theory. A period of six weeks immediately following the first four months' instruction in General Chemistry is devoted to work of this nature."

The subject is divided in the table of contents as follows: outline of leading principles and common conventions pertaining to the study of general inorganic chemistry; natural classification of the elements; determination of the molecular weights; determination of atomic weights; calculation of formulas; osmotic pressure and related phenomena with particular reference to dilute aqueous solution of acids, bases and salts; the electrolytic dissociation theory; the law of chemical mass action; heterogeneous equilibrium; thermochemistry.

A good deal of this is already included in the ordinary introductory course. Whether the rest of it should be included is a matter for experiment and cannot be decided on *a priori* grounds. It is unquestionably a good thing to have the experiment tried in as many ways as possible. The reviewer feels certain,

however, that the author goes too far when he deduces the gas laws from the kinetic theory of gases. Under no conceivable circumstances can such a deduction be of value to a freshman.

It is not true as stated on p. 20, that "a saturated solution contains the maximum amount of material which will dissolve at the given temperature." There is some question also as to the accuracy of the statement on p. 21 that "excessive solubility of a gas in a liquid is due to chemical action." Such a statement is certainly out of place in a text-book for freshmen. The effect of environment appears on p. 90. Nowhere outside of the Yale laboratory would the double bromide of caesium and lead be cited as a typical well-known double salt. So long as there is any possibility of the student learning the facts in regard to potassium nitrate and sodium nitrate, the reviewer believes that it is dangerous to lay too much stress on the quantitative precipitating action of the common ion. The reviewer is naturally hopelessly out of sympathy with the statement on p. 114 that "obviously the phase rule is chiefly important as an instrument for indicating the numerical relation between the number of components and the number of phases, which must characterize this preeminently definite condition of equilibrium." It would have been more accurate to have said that the phase rule is chiefly important as a basis for classification and as an instrument of research. *Wilder D. Bancroft.*

Die englischen elektrochemischen Patente. *By P. Ferchland. Auszüge aus den Patentschriften (Monographien über angewandte Elektrochemie XXXII. Band). Zweiter Band: Elektrothermische Verfahren und Apparate; Entladungen durch Gase. 17 × 23 cm; pp. 190. Halle: Wilhelm Knapp, 1908. Price: paper, 9.50 marks.*—The first volume (12, 648) contained only those patents relating to electrolysis. This volume contains the electric furnace patents and those on electrical discharges through gases. The book contains practically all the patents granted up to the end of 1906 and also nearly all of those for which application was made during 1907. The book is distinctly valuable for reference. Some names are mis-spelled as Thompson for Thomson, and Brindlay for Brindley; but such mistakes as these do not shake one's confidence in the general accuracy of the text. *Wilder D. Bancroft.*

Elektrolytische Zähler. *By Konrad Norden. (Monographien über angewandte Elektrochemie. XXXI. Band.) 17 × 24 cm; pp. ix + 166. Halle: Wilhelm Knapp, 1908. Price: paper, 9 marks.*—An electrolytic meter can only measure current and we cannot get kilowatt hours from it unless we postulate a constant voltage. For this reason and also for others, the electrolytic meter, though first in the field, is now of relatively small importance. The author estimates that only about five percent of the meters in Europe belong to this type. No figures are given for the United States; but it is pretty certain that the electrolytic meter is a negligible item in this country.

The author believes that there may perhaps be a commercial future for some form of the electrolytic meter and he has written this book to show what has been done in this line. It is a valuable compilation and it is always interesting to know how a problem has been attacked even though the problem itself may have more of a past than a future. *Wilder D. Bancroft*

THE ELECTROCHEMISTRY OF LIGHT. VI

BY WILDER D. BANCROFT

The Problem of Solarization. Part III

When a flash of lightning is photographed, it often happens that some portions of the flash are reversed on the negative, the effect depending to a certain extent on the treatment which the plate receives. This special reversal was first observed by Clayden[1] in 1899, and is known as the Clayden effect. The factors which play a part in this phenomenon were studied by R. W. Wood.[2]

"Mr. Clayden showed that if a plate which had received an impression of a lightning flash or electric spark was subsequently slightly fogged, either by exposing it to diffused light or by leaving the lens of the camera open, the flash on development came out darker than the background. If, however, the plate was fogged before the image of the flash was impressed, it came out brighter than the background, as in the ordinary pictures of lightning. I refer to the appearance in the positive print in each case. This is quite different from ordinary reversal due to the action of a very intense light, for the order in which the lights are applied is a factor, and the phenomenon lies wholly in the region of under-exposure. I repeated Mr. Clayden's experiment, and obtained dark flashes without any difficulty.

"The effect cannot, however, be obtained by impressing an image of the filament of an incandescent lamp on a plate, and subsequently fogging the plate. Clearly there is something about the light of the electric spark which is essential to the production of the reversal. It is not intensity, however, for I found that it was impossible to obtain reversed images of bright sparks with the lens wide open.

[1] Cf. Eder's Jahrbuch der Photographie, 15, 610 (1901)
[2] Nature, 61, 104 (1899).

"Fig. 1[1] shows a series of spark images, some normal, some partly reversed, and others wholly reversed. The sparks are those of a large inductorium with a good-sized Leyden jar in circuit. The sparks were all of equal intensity, but after each discharge the iris diaphragm of the lens was closed a little. It will be seen that the borders of the bright sparks are reversed. In some the image is reversed, with the exception of a narrow thread down the core. The images were impressed in succession on the plate by moving it in the camera. A plate holder was dispensed with, an opening being made in the ground-glass back by removing a strip a few centimeters wide. The plate was held against this opening, and a large number of exposures made in a few minutes. Of course, the room was in total darkness. After exposure, the plate was exposed to the light of a candle for a second or two, and then developed.

"In this series of pictures it will be seen that the edges of the bright images of the sparks are reversed, the intensity on the border of the image being less than at the core. As the intensity of the spark becomes less and less, the bright central core dwindles down to a mere thread, and eventually disappears, the spark's image being feeble enough to reverse over its entire area.

"This explains why the dark lightning flashes are usually ramifications of the main flash. The ramifications are less brilliant discharges and reverse, while the main one is too bright to cause the effect.

"The first thing that occurs to one is that it may be some peculiar radiation, which the spark emits, which is wanting in the light coming from other bodies. If a small photographic plate is partly screened by a piece of black paper and illuminated by the light of a small spark at a distance of two or three feet, and a similar plate, screened in the same manner, is illuminated for a moment by candle light of sufficient intensity to produce the same amount of blackening on

[1] [The cuts referred to in the text are not reproduced in this paper.]

development, we shall have the means of showing that the spark light differs in its action on the plate from that of the candle. If these two plates, before development, be half-screened in a direction at right angles to the former one, and exposed to the light of the candle for a second or two, the part of the plate which has been illuminated by spark light plus candle light does not become as black on developing as the part which has received candle light alone, whereas the part which has been twice exposed to candle light is blacker than that which has been only exposed once. This shows that the light of the spark does not act in the same way as the light of the candle. Wherein does it differ? It seemed possible that the peculiarity lay in the nature of its radiation. To test this a prism was placed before the lens of the camera, which broke up the image of the spark into a series of spark images of different color. The plate was exposed to the flashed spectrum of a single spark, then removed from the camera and exposed to the candle light, and developed. If the reversing effect was due to any peculiar radiation or wave-length we should find the reversal at that part of the spectrum where the effective radiation belonged, say in the infra-red if the reversing power lay in long waves given out by the spark. It was found that the entire spectrum came out lighter on the negative than the fogged background. A second plate was exposed to the spectrum flash, then slightly fogged, and a second spectrum impressed on it in a different place. On developing, one spectrum came out light and the other dark. Clearly the effect does not depend on wave-length. It then occurred to me that the time-element might enter into the problem. The light of the spark is over in about 1/50000 of a second, and it did not seem impossible that a bright light of exceedingly short duration might act quite differently on a plate from a weaker light of longer duration. This may be tested in a variety of ways. We may open the lens wide, impress the image of a single spark on the plate, and then stop the lens down and superimpose a number of spark images sufficient to make the total exposure the same

in each case. This was the first method which I tried. In order to compel the successive sparks to pass over the same path, that their images might be superposed, I shut them up in a capillary tube. With the lens open wide enough to give the maximum reversing action, I passed a single discharge through the capillary. Stopping the lens down to one quarter of its former aperture, four discharges were passed through the tube. The plate was then fogged in the usual manner, and on development the single discharge was reversed, but the composite one was not.

"Fig. 2 is from a plate showing this effect. The upper images are those of single discharges through the capillary, with different apertures of the lens; the lower images are those of double or triple discharges through the same tube. The left-hand side of the plate was exposed to the candle light for different amounts of time, by moving the screen over small distances during the exposure. Only the single discharges reverse, though the intensity of the images on the unfogged portion of the plate is the same.

"This was strong evidence that the duration of the illumination was the important factor. Some years ago I measured the duration of the flash of exploding oxy-hydrogen, finding it to be about 1/12000 of a second. Possibly the flash of such an explosion would duplicate the effect. I exploded several glass bulbs with electrolytic gas, but found that the action was the same as that of ordinary light, it being impossible to get any reversal. The flash evidently lasted too long, or there still remained some undiscovered factor."

"To demonstrate conclusively that the time-factor was the only one, it was necessary to secure an illumination independent of the electric spark, and of as short duration. This was accomplished in the following manner: A disc 30 cms. in diameter was furnished with a radial slit 1 millimeter wide near its periphery, and mounted on the shaft of a high-speed electric motor. A second slit of equal width was arranged close to the rim of the disc, in such a position that

the two slits would be in coincidence once in every revolution. This second slit was cut in the wall of a vertical chute, down which a photographic plate could be dropped. By means of a large convex lens of short focus, an image of the crater of an arc-lamp was thrown on the point of coincidence of the slits. The intensity of the illumination transmitted by the slits when in coincidence was almost sufficient to char paper. The motor was now set in motion, and a plate dropped down the chute. On developing this plate, three images of the slit appeared, not all over-exposed, though the plate was the fastest obtainable, and the intensity of the light while it lasted comparable to that at the focus of a burning glass. By measuring the distance between the images and the vertical distances through which the plate had fallen, it was an easy matter to calculate the speed of rotation, which was found to be sixty revolutions per second, the air friction of the disc preventing higher speed. The duration of the exposure will be the time occupied by the rim in travelling a distance equal to the width of the slit, or 1 mm. This was found to be 1/55000 of a second, about that of the spark. The crucial experiment now remained. A second plate was dropped, and, before development, was exposed to the light of the candle. The images of the slit were most beautifully reversed, except at the center, where the light was too intense. It seems, then, that we are justified in assuming that the action of an intense light on a plate for a very brief time-interval decreases the sensitiveness of the plate to light. It is curious to contrast with this effect the fact that exposure to a dim light for a moment or two appears to increase the sensibility by doing the small amount of preliminary work on the molecules, which seems to be necessary before any change can be effected that will respond to the developer.

"I am not prepared to say what the nature of the change effected by the flash is. Possibly some one familiar with the theory of sensitive emulsions can answer the question. I have tried using polarized light for the reversing flash, and then fogging out one-half of the plate with light polarized in

the same plane, and the other half with light polarized at right angles to it. As was to be expected, there was no difference in the effects."

What seems at first sight to be another form of reversal was observed by Trowbridge.[1]

"In passing from the study of the light emitted by gases under the effect of electrical discharges to the investigation of the light produced by discharges of great quantity, one enters a new field of research. In previous papers on the spectra of hydrogen I have stated my convictions of the importance of the rôle played by water-vapor in glass spectrum-tubes. The results of further study emphasize these convictions. With powerful discharges in hydrogen, oxygen, and rarefied air, even when these gases are dried with the utmost care, I always obtain the same spectrum, which I regard as that arising from the dissociation of water-vapor which is always present in glass tubes. The bright-line spectrum, moreover, at high temperatures is accompanied by a faint continuous spectrum on which are dark lines which indicate a selective reversibility in the silver salt. This reversibility, it seems to me, is of great significance in the application of photography to astrophysics.

"It has long been recognized that spectrum analysis is an extremely delicate method of recognizing the presence of a gas or the vapor of a metal under the excitation of heat; and when the improvements in the photography enabled us to obtain permanent records of the spectra of gases, it was supposed that we had a means of escaping from the fallacies of eye-observations which arose from personal idiosyncracies. If the photographic plate were a perfect instrument for recording the infinite number of vibrations which light can communicate to atoms of matter, we should certainly feel that we had made a great advance in physical science. When we reflect, however, on the supposition that emulsions containing silver salts are capable of responding and giving a

[1] Phil. Mag. [6], **4**, 156 (1902).

permanent record of all waves of light, even in the portion of the spectrum considered most actinic, when the waves exceed a certain intensity, we are conscious that we rely without proof upon an infinite range of photochemical action; and indeed I show in this paper the existence of a selective reversibility produced on the photographic plate by powerful discharges producing light of great intensity.

"When we turn to powerful discharges through Plücker or Geissler tubes filled with hydrogen which has been dried with care, we also obtain a faint continuous spectrum on which are bright lines and dark lines. Moreover, what are apparently the strongest bright lines of the dissociation-spectrum of water-vapor are not reversed. There is a selective reversibility which arises at high temperatures.

"This fact seems to me of great importance in the application of photography to the study of celestial phenomena. Reversal of spectrum lines does not necessarily indicate reversing layers of cooling gases, and in certain cases may arise from photo-chemical action of the silver salt. One immediately thinks in this connection of the phenomenon of dark lightning or the Clayden effect, and of the interesting experiments of Professor Nipher. Spectrum analysis, however, reveals a selective reversibility which must be carefully studied before we can properly interpret the records of photography. There are doubtless many states of vibration, even in the actinic portion of the spectrum, which are not recorded by the silver salt, for this selective reversibility may obliterate or prevent a permanent record. I have obtained this reversing action with different emulsions on glass and also on celluloid films. The strongest reversals are approximately at wave-lengths 4227, 3930, 3965. There is also a faint reversal at wave-length 3953. Reversals are often seen on the negative which disappear in the fixing-bath.

"In this investigation, ten thousand cells were employed to charge a glass condenser of 0.6 microfarad. The charge was sent through Geissler tubes with practically

no self-induction in the discharge-circuit. The bore of the capillary tubes was 1 mm., and the tubes were filled with apparently dry hydrogen at a pressure of approximately 0.1 mm. The tubes were also filled with oxygen and also with rarefied air at the same pressure. I have reached a limit in subjecting glass tubes to powerful discharges, and am now turning my attention to obtaining quartz tubes in the hope of securing a more resisting material.

"In a previous paper I expressed my conviction that the four-line spectrum observed in the protuberances of the sun is an evidence of the presence of water-vapor in the sun's atmosphere, and an evidence, therefore, of the presence of oxygen. In the spectrum one sees on the negative two reversed lines which coincide with the great H,H lines of the solar spectrum. These are seen bright in B, Fig. 4.[1] One also sees a strong reversed line at approximately wave-length 4227; and there is a reversed band coinciding with the solar region of reversed lines between wave-lengths 4315–4285. These regions in the sun are doubtless composite photographs of reversals of many elements. I believe that there is a basis of reversal due to the dissociation of water-vapor.

"The nomenclature of the stars in regard to their types of spectra may need revision. The higher temperature I get, the more dark lines I obtain.

"An excess of dissociation of water-vapor may suffice to give at a comparatively low temperature the bright-line spectrum of hydrogen. At higher temperature the dissociation of this vapor in the presence of atmospheric air may give dark lines. The intense light due to the dissociation of water-vapor under the effect of powerful discharges is the nearest approach to sunlight which I have been able to produce. Its actinic effect is greater than that of magnesium, zinc, or aluminum. It may be that the variability of certain stars is due to a variability in the amount of water-vapor which is being dissociated; and one is led to conjecture whether the

[1] [Not reproduced in this paper.]

light of the sun's atmosphere may not be due to an electrical dissociation. The selective reversibility of the silver salts seems to me, therefore, of great importance in the subject of astrophysics, for we can have reversible effects on the photographic plates which are not due to the reversing effect of colder layers of gases. In other words, we have actions recorded which are on the plates and not in the heavens. The intense light due to the dissociation of water-vapor may entirely mask the fainter light of the metallic lines in stars which show only gaseous spectra, especially when we consider the varying distances of the stars. I have employed electrodes of platinum, copper, silver, aluminum, iron, and found no trace of the lines of their vapor in the spectrum of the dissociation of water-vapor. Even when caustic soda is present in the tubes, although it fills the tube with a brilliant yellow light with comparatively low discharges, no trace is seen of it when the tube is excited with powerful discharges. Then we have the brilliant white light of the water-vapor spectrum.

"The silver salt, therefore, does not respond to all rates of vibration; or if it does respond, the molecular action is unstable and there is no resultant reaction which is evidenced by a photographic image. There may be spectra at very high instantaneous temperatures which we cannot photograph. It seems reasonable to suppose that the silver molecule is limited in its rate of vibrations, and that the photographic plate as well as the human eye is a limited instrument of research."

These phenomena have been studied more in detail by R. W. Wood.[1]

"The importance of distinguishing between photographic and true reversals of lines in spectrograms has made it seem worth while to investigate with some care the conditions under which reversals due entirely to photographic action can occur. Professor Trowbridge[2] has advanced the theory

[1] Phil. Mag. [6], 6, 577 (1903).
[2] [Ibid. [6], 4, 160 (1902)].

of selective reversibility of the silver salts in the sensitive film for certain wave-lengths, and it was in part to determine whether the tendency of a line to reverse was a function of the wave-length, that the present investigation was undertaken.

"As I showed several years ago, the Clayden effect, or the type of reversal giving rise to the phenomenon of dark lightning, results from the action of a light-shock on the plate before its exposure to diffuse light. The effect of this light-shock, which must be of very brief duration, is to decrease the sensibility of the plate, resulting in a less energetic action during the subsequent illumination. I made no attempt at the time to determine the maximum duration of the light shock which would still give the Clayden reversal, but expressed the opinion that it could not exceed 1/10,000 of a second. This opinion was based on a single experiment, and I have since found that by a suitable adjustment of the conditions the duration may be as great at 1/1000 of a second, though only a very slight trace of reversal occurs under these conditions.

"It appears to me now that there are at least four different types of photographic reversal, or perhaps five if we allow the chemical treatment of the plate between two exposures. As any one of these four types is liable to occur in any photographic work, when the proper conditions are fulfilled, it may be well to enumerate them at the beginning.

"*First Type.*—The ordinary over-exposure reversal, which occurs when the plate is given three or four hundred times its normal exposure and then developed in the usual way.

"*Second Type.*—The reversals produced by developing the plate in full lamp-light, the plate having been more or less over-exposed to begin with. This type has been extensively studied by Nipher, the results of his experiments being given in the Proceedings of the St. Louis Academy of Science.

"*Third Type.*—This type must occur frequently, though

I never remember to have seen it described. It happens when a normally or under-exposed plate is developed and then exposed to light for a minute or two before the hypo bath. The fogging, which is usually of a reddish-brown color, does not occur on the portions of the plate where there is a developed image, and even if this image is very feeble it remains clean and almost transparent. I first noticed this effect in some photographs of spectra which showed strong reversals along the edges where the illumination must have been very feeble, and was unable to explain it. Further experimenting showed that it had resulted from turning up the light before the plate had been thoroughly fixed. Doubtless this effect has been described time and again in the photographic journals, but it was new to me, and may be to some others. Reversals of this type will be seen in Fig. 6 illustrating my paper on screens transparent to ultra-violet light.[1] The spectra (negative) have brighter borders.

"*Fourth Type.*—The Clayden effect which is the type chiefly to be dealt with in the present paper. This occurs when an exposure of about 1/1000 of a second or less is given, and the plates subsequently fogged by exposure to diffuse light before development. If images of electric sparks are thrown on a plate and the plate then exposed to the light of a candle for a few seconds, the spark images will develop reversed, which is not the case if the exposure to candle-light precedes the impression of the spark images.

"This effect is shown in Fig. A.[2] A series of spark images have been gradually reversed by exposing the plate in strips to the light of a candle. The upper strip was exposed 30 seconds, the following 20, 15, 10, 5, 2, 0 respectively.

"*Fifth Type.*—I have found that the condition produced in the sensitive film by light shock can be imitated by treating the plate, after exposing portions of it to the action of a feeble light for a few seconds, to an oxidizing bath of bichromate of potash and nitric acid. If the plate is dried and

[1] Phil. Mag., February, 1903.

[2] [The figures referred to in the text are not reproduced in this article.]

then fogged by candle-light and developed, the previously exposed portions will come out reversed.

"This effect is shown in Plate XXVI, Fig. 4. A series of spark images were impressed on the plate, which was then covered with a piece of black paper in which a narrow slit had been cut. A number of images of this slit were then impressed on the plate by exposure to the light of a candle. If the plate in this condition was then fogged by candle-light and developed, the spark-images would come out reversed and the slit images not reversed. Before fogging it, one end (the upper in the print) was immersed for a few minutes in a very dilute solution of bichromate of potash, slightly acidified with nitric acid. It was then dried, exposed to candle-light and developed. In the lower portion of the print we find the sparks black and the slit images white; in the upper portion both sets of images come out dark, the reversal of the sparks being much stronger than on the untreated portion of the plate.

"In the present paper I propose to discuss the Clayden effect not only in connection with the selective reversibility hypothesis adopted by Professor Trowbridge to explain his spectrum photographs, but also in relation to the time factor, and radiations other than light, such as the Becquerel and Röntgen rays, which are quite different in their action from light.

"I shall, in dealing with the subject, speak of the initial exposure of brief duration as the light-shock. The subsequent illumination which causes the reversal of the impression of the shock, I shall call the fogging exposure.

"The first subject investigated was the relation of the phenomenon to the wave-length of the light. The light shock in this case was administered by exposing the plate to the spectrum of one or more sparks between cadmium electrodes by means of a small quartz spectrograph. Even with a small diaphragm the illumination by a single spark yielded a developable image of the spectrum down to the extreme ultra-violet. Six spectra were impressed on the

same plate with different sized diaphragms; the plate was then exposed to the light of a candle for a few seconds and developed, the result being produced in Plate XXVI, Fig. 1. It will be seen that the lines and the continuous background come out positive in the two upper spectra, showing that if the shock is too intense no reversal takes place, a circumstance in which the Clayden effect differs essentially from ordinary reversal due to over-exposure. Professor Trowbridge says that his reversals occur where bright lines fall on a continuous background, and considers the reversing action proportional to the product of the two effects. If his reversals are of this nature this cannot be the case, for by making one factor (the light shock) large, no trace of reversal appears. As I shall show presently, this statement requires some modification, for, as we increase the intensity of the shock, we can by increasing the fogging exposure still get reversal. As I said in my previous note, it appears probable to me that in Professor Trowbridge's photographs of spectra of single sparks, the shock was the almost instantaneous exposure to a bright-line spectrum of exceeding brief duration, followed by an exposure to a superimposed continuous spectrum of longer duration, which may have been due to incandescence of the inner wall of the capillary tube, or to phosphorescence of the gas. By employing a tube with a bore of about 0.25 mm. I have obtained reversed lines in the blue with the single discharges of a medium-sized induction-coil and condenser.

"The fact that the faint continuous spectrum of the spark is uniformly reversed shows that there is no selective reversibility so far as the initial light-shock is concerned.

"I next endeavored to determine whether the wave-length of the fogging-light had anything to do with the matter (in which case we should expect reversals in some parts of the spectrum and not in others), in the particular case where the fogging illumination was spread out into a spectrum as in Professor Trowbridge's photographs. Having already found that fogging the plate with X-rays never gave reversals

of spark images, it occurred to me that possibly ultra-violet light might act in a similar manner. Having impressed a number of spark images on a plate, it was illuminated with light of wave-length in the neighborhood of $\lambda = 23$, from a discharge between cadmium electrodes, a screen provided with a slit being placed in the focal plane of the quartz spectrograph, with the plate of a short distance behind it. The spark-images were not reversed, and it appeared at first sight as if ultra-violet light of this wave-length acted like the X-rays. I was, however, not willing to accept this conclusion without further study, since the fogging illumination in this case consists in reality of a number of feeble light-shocks, that is, it is of much briefer duration than in the case of candle-light. In the first experiment the fogging illumination by ultra-violet light was produced by the passage of perhaps a score of sparks before the slit of the spectrograph. To get a feebler illumination of longer duration I moved the next plate to a distance of about two meters from the screen and let the coil run for about a minute. The room was absolutely dark, the spark-terminals and the front of the spectrograph being covered with a heavy black cloth, so that the only light that reached the plate was of the wave-length above mentioned. On this plate the spark-images, which had been previously impressed were strongly reversed showing that the time factor comes in the fogging light as well as in the light-shock, and that ultra-violet light is as efficient as any other, if it is not of too brief duration. This appears to dispose of the idea of selective reversibility, at least so far as the Clayden effect is concerned.

"*Investigation of the Time Factor.*—To determine the maximum duration of time which the light-shock may have and still reverse, the following method was used: A disk of cardboard 50 cms. in diameter was mounted on the shaft of an electric motor, the speed of which could be determined by the tracing of a tuning-fork on a smoked metal plate mounted on the same shaft. Near the rim of the disk a number of narrow slits were cut, varying in width from 1 mm. to 5

mms. An arc-light was focused on the rim by means of a large condensing-lens, the image of the crater being about half a millimeter in diameter. By driving the disk at a high rate of speed, intermittent flashes of very brief duration were obtained as the slits passed across the arc's image. A short distance behind the disk, a rectangular metal tube was mounted provided with a slit 1.5 mm. wide, immediately opposite the point where the image of the arc fell on the disk. Down this tube the plate was dropped, receiving in its passage before the slit light flashes of varying duration. The plate was subsequently exposed to candle-light and developed. The images of the slit in the case of the briefest flashes were perfectly sharp, in the other cases they were broadened owing to the rapid motion of the plate. This made the interpretation of some of the records difficult, and it was found better, when working with flashes longer than 1/2000 of a second in duration, to lower the plate down the tube with a thread. A print from one of these plates is shown in Fig. 2, Plate XXVI. In this case there were two 1 mm. slits on the rim of the disk not very far apart, then a slit somewhat wider further around, and after this a still wider one. It will be seen that the slit images formed by the two very short flashes are completely reversed, while the others are only reversed on their edges.

"If the plate moves during the exposure, as was the case in this photograph, it is obvious that the edges of the slit-image will receive less exposure than the center, which accounts for the partial reversal. As the results of exposing about two dozen plates, it was found that the duration of the shock could be as long as 1/1000 of a second, and still yield reversals. It was only by carefully regulating the intensity of the fogging-light and the duration of the development that these reversals could be obtained.

"When the duration is less than 1/2000 sec. reversals could be obtained without difficulty. Flashes varying in duration from 1/15,000 sec. to 1/500 sec. were studied, and it was found that as the duration of the shock was increased

the reversals became weaker, the images finally failing to appear at all on the plate, notwithstanding the longer duration of the flash. On still further increasing the duration, the images came out not reversed. There may be some connection between the condition in which the light shocks fail to develop at all, and the zero condition of the plate described by Nipher.

"The experiment in which the fogging of the plate was effected by exposure to ultra-violet light furnished by a quartz spectrograph shows that the time factor plays a rôle in the fogging-light as well as in the light-shock.

"It was found that if the fogging light was rather intense but of short duration, the image of the light-shock did not reverse; if the light was less intense, but of a little longer duration, no trace of the shock appeared, while if the light was still less intense, and of somewhat longer duration, the image came out reversed. With a suitable ratio of intensities and durations of time, it is possible to superpose two impressions on a photographic plate, only one of which appears on development.

"This effect was shown in Fig. 3, Plate XXVI. A series of spark-images of equal intensity was impressed on the plate, which was then fogged in sections, the lower strip being exposed to the light of one spark at a distance of a meter, the next to the light of four sparks at a distance of two meters, the next to nine sparks at three meters, and so on. The total amount of fogging-light was thus approximately the same in each case, though it was found that considerably greater action was produced by a larger number of sparks at a considerable distance, than by a single spark close to the plate. It will be noticed that on the third strip from the bottom there is scarcely a trace of the spark-images. The ratio of the times of duration of the shock and the fogging-light was in this case about 1:9. On the two strips below this one, the sparks appear not reversed, while on all of the strips above reversal has taken place.

"A more careful quantitative investigation of these

effects is much to be desired, with apparatus of such design that the duration and intensity of both the light-shock and fogging-light can be accurately controlled.

"I am of the opinion that the result of such an investigation would be the establishment of the fact that with very brief and intense light-shocks, comparatively intense fogging-light of short duration will yield reversals, while in the case of shocks of say 1/1000 sec. duration, the fogging-light must be feeble and of long duration in order that reversals may be obtained. My plates appear to indicate this qualitatively, but quantitative data could doubtless be obtained with suitable apparatus. As I shall show later, it is possible to administer the shock in such a manner that it comes out reversed even when the fogging-light is the flash of a single spark.

"I have tried to obtain some idea of the action of the light-shock by attempting to transform its effect on the plate into an effect similar to that produced by ordinary exposure, by means of the action of various chemical agents. These experiments were all failures, but the interesting fact was ascertained that an ordinary exposure appeared to be transformed into a shock exposure by the action of a dilute bath of bichromate of potash slightly acid with HNO_3. This effect is shown in Fig. 4, Plate XXVI. A series of spark-images was impressed on the plate, and then a series of images obtained by illuminating the plate with the light of a candle shining through a slit in a piece of black paper. One-half of the plate was then dipped into the bath, washed and dried, exposed to the light of a candle, and developed. A print from this plate is reproduced in Fig. 4, Plate XXVI. On the upper portion, which was treated with bichromate, both the spark-images appear reversed, on the lower, the latter are not reversed. This experiment merely shows that a plate which has been exposed to light in certain places and then treated to the bichromate solution, is less sensitive to the action of subsequent illumination on the spots which have previously received light. The condition may appear

at first sight to be similar to that produced by a light-shock, but there is in reality probably no connection between the two, for while light-shocks not followed by fogging can be developed as not reversed images, the "bichromatized images" do not develop at all unless the plate is fogged before development.

"The nearest approach which I have been able to make to the transformation of the effect of a light-shock into that due to ordinary exposure, is by the action of the X-rays. It was found that spark-images could not be reversed under any circumstances if the plate was fogged by these rays instead of candle light. To prove that the case was not analogous to the one in which ultra-violet light failed to give reversals, owing to the comparatively brief duration of the illumination, long exposures were made with the X-ray tube at a considerable distance. Not only were reversals never obtained, but it was found that after a brief exposure to the rays, fogging the plate by lamp-light failed to reverse the spark-images. This seemed very remarkable, for it was subsequently ascertained that X-ray images could be reversed even when produced by long exposure to feeble radiation, by subsequent exposure of the plate to lamp-light. This effect is shown in Fig. 5, Plate XXVI.

"The spark-images were impressed first. The plate was then exposed in vertical strips to the action of X-rays for varying lengths of time, the left-hand strip receiving the longest exposure, while the right-hand strip was not exposed at all. Following this came an exposure in horizontal strips to lamp-light, the lower strip having the longest exposure and the upper one having none at all. It will be seen that there is no trace of reversal in the upper left-hand corner, where the fogging is due almost wholly to X-rays, while reversed edges appear on all of the sparks in the lower right-hand corner, where the fogging was due to light: moreover, in the lower left-hand corner, where the X-ray fog preceded the light fog, the images were not reversed. On investigating the matter further, I found that shocks administered by

single powerful flashes of X-rays were reversed by subsequent exposure to lamp-light. In this case, however, the time element appears to be without much influence, for images formed by long exposure to very feeble X-radiation reverse in the same manner. This seems very remarkable, when we consider the fact that exposure to these rays changes the condition produced by light-shock in some manner, so that it is impossible to reverse it by further fogging.

"The reversal by X-rays is illustrated in Fig. 6. A plate was wrapped up in black paper and exposed to the radiation for several minutes, a vertical iron rod shielding the center strip of the plate. The plate was then exposed to lamp-light for different lengths of time in strips perpendicular to the shadow of the iron rod. On development it was found that on the end of the plate which had received the shorter exposures to light, the central strip came out lighter than the background, while on the opposite end of the plate it was darker. At a certain point near the center of the plate, all traces of the shadow of the rod had disappeared, showing that exposure to X-rays for some time, and then to light for certain time, produces an image no blacker than the light alone would have produced.

"I next ascertained that if the plate be exposed simultaneously to light and X-rays, the latter inhibit the action of the former. A candle and an X-ray tube were set up at some little distance apart in front of a plate, the latter being much nearer the plate however, owing to its less energetic action. An iron rod mounted in front of the plate cast two shadows upon the sensitive film, one a light shadow, the other an X-ray shadow. After the double exposure, the plate was developed, with the curious result that one shadow was darker than the background, the other lighter, showing that the light was more energetic in its action on the area screened from the X-radiation.

"It may be worthy of mention that both this result and the preceding one were predicted before the actual experiments were tried. The prediction was the result of an

attempt to apply Bose's strain theory of photographic action[1] to the phenomena in question. This theory seemed rather promising at first, especially as it enabled me to predict new phenomena, but it failed to account for so many things that I was finally forced to abandon it.

"The action of the other stimuli was next investigated. It has long been known that pressure-marks on the film can be developed. I found that if the plate was fogged by lamp-light before developing, the pressure-marks came out reversed. It then occurred to me to try the effect of light shocks on pressure-marks, and I found to my surprise that the flash of a single spark was as effective in reversing the pressure-mark as the exposure to the lamp. The pressure-marks can also be reversed by exposure to X-rays.

"As a result of numerous other experiments, I finally found that if we arrange the stimuli in the following order, pressure-marks, X-rays, light-shock, and lamp-light, an impression of any one of them can be reversed by subsequent exposure to any other following it in the list, but under no circumstance by any one preceding it. For example, pressure-marks can be reversed by any of the other three stimuli, while X-ray images are only reversed by light-shock and lamp-light.

"Experiments with Becquerel rays have given rather uncertain results. Pressure-marks can be reversed by them, and they in turn can be reversed by lamp-light, but these were the only two cases in which reversals were obtained, which makes it difficult to fit the rays into the series and still have the rule hold.

"These experiments show that the effects of the different kinds of stimuli on the sensitive film are quite different. Much more experimental work will have to be done before any definite notion can be obtained as to the nature of the changes produced by the action of radiation of any sort, and it is hoped that the experiments described in this paper

[1] J. C. Bose: Proc. Roy. Soc., June 19, 1902.

may prove suggestive to others. Doubtless an exhaustive study of the action of various chemical agents on the plate between the two exposures would throw much light on the cause of the reversals.

"If I interpret the strain-theory correctly, the application to these phenomena would be to assume that the light-shock produces a negative strain, while lamp-light produces a positive strain, either of which yields an image on development. The reversal in cases where the lamp-light follows the impression of the light-shock could be explained by assuming that the negative strain has to be undone before the positive strain can begin, consequently these parts of the plate lag behind the parts which have not received the light-shock. We should then assume that the positive strain once started can be continued by a stimulus which, acting first, would have produced a negative strain, in order to account for the fact that exposures to lamp-light are not reversed by light-shocks. Moreover, it is difficult to explain on the strain-theory that two different stimuli acting in succession may produce only the same effect as one of them acting alone. It appears to me that the strain-theory would lead us to suppose that the negative strain produced by the first stimulus might be exactly neutralized by a stimulus which produces a positive strain, the plate returning to its original condition, *i. e.*, not darkening on development. This is never the case.

"In cases where reversed lines appear in the spectrum, which are suspected of being photographic in origin, *i. e.*, not true absorption-lines, the following precautions should be taken. Repeat the exposure a number of times, using successively smaller diaphragms before the prism. If the reversal is ordinary solarization, due to over-exposure, it should disappear when the intensity of the light is sufficiently reduced. It seems to me that in such cases the reversed line should be bordered by bright edges, which does not seem to be the case in the photographs published by Professor Trowbridge. If the Clayden effect is suspected, the source

of light should be examined with a revolving mirror, to determine whether a dual illumination is present. The speed of the mirror should not be too great, otherwise the phosphorescence, if it exists, may be spread out to such an extent that no trace of it appears. This may account for the failure to obtain evidence of a dual illumination in the case of heavy discharges in quartz tubes."

In a paper, recently published, B. Walter[1] calls attention to the fact that different observers have reported very different values for the ratio between the time of exposure necessary to produce any latent image at all and the time of exposure which gives the maximum blackening when the plate is developed. Thus Ebert[2] found a ratio of 1 : 5000, Precht[3] one of 1 : 200000 and Scheiner[4] one of about 1 : 400. Careful experiments showed that these discordant results were due to differences in the plates used. Walter concludes "that photographic plates from different makers differ extraordinarily in their tendency to solarization even when the sensitiveness is the same. In fact there is no connection between sensitiveness and the tendency to solarize. The order in which plates from different makers solarize, is different for Röntgen rays from that for light rays and there is still a third order for the Clayden effect. When different developers were used, but the development continued for a normal time, the beginning of solarization, *i. e.*, the moment of maximum blackening, occurs always at approximately the same exposure, though the absolute value of the blackening may be very different.

The author believes that all the experimental results can best be explained "along the lines of Abney's theory, by the assumption that with increasing time of exposure the silver bromide molecule passes through at least *two* qualitatively distinct phases, the first of which is the one which is

[1] Drude's Ann., **27**, 83 (1908).
[2] Eder's Jahrbuch der Photographie, **8**, 14 (1894).
[3] Phys. Zeit., **3**, 426 (1894).
[4] Populäre Astrophysik., 313 (1908)

reduced by the developer while the second is less readily reduced. According to this view the maximum blackening obviously occurs when the exposure has been such that the greatest possible number of the silver bromide particles is in the first decomposition stage, which will therefore be independent of the nature of the developer. The absolute blackening of the plate may, however, be different in the different developers, for these do not need to have the same reducing powers.

"The established fact, that there is no connection between sensitiveness and the tendency to solarize, seems to be a reason for believing that the action of light cannot consist in a continuous uniform change but that the solarization is marked by the formation of a third phase completely different from the second phase of silver bromide which is reduced by the developer.

"The very different tendencies to solarization of plates having the same sensitiveness are perhaps due to the fact that the methods of preparing the emulsions differ in different factories and that this affects the formation of the second phase in the decomposition of silver bromide though not the first. In favor of this view is the previously mentioned fact that plates from the *same* factory usually show only slight differences in the matter of solarization, even though they may differ very much in sensitiveness."

Although agreeing in the main with Abney's theory the author does not think that it has been proved that the two phases are a sub-bromide and an oxy-bromide. In a long paper by Trivelli,[1] the final conclusion is quite a different one, namely that Abney's explanation is not a satisfactory one at all.

"The existing nomenclature is such that several conceptions are grouped under a single name. This produces confusion and makes it necessary to define our terms more closely.

[1] Zeit. wiss. Photographie, 6, 197, 237, 273 (1908).

"When studying the gradation of the blackening we may expose a photographic plate in two ways:

"(*a*) With constant intensity of light and varying time of exposure;

"(*b*) With simultaneous illumination by lights of different intensities.

"In order to eliminate changing conditions especially during development, the first method is usually so carried out that the plate is exposed in stages. This constitutes in a sense a combining of several experiments into a single one. According to my view one cannot speak here of the appearance of an image.[1] We only get that by the second method.

"I shall give the name of *copies* to the results obtained by simultaneous illumination with lights of different intensities. A copy always shows an image, which may however be positive or negative.

"If the object to be photographed is a positive, the plate, which is obtained by an ordinary exposure in the camera, develops as a negative. In a printing frame we get a positive from this negative, and so on. I call these copies *unpolarized* or *normal*, and this copying may be represented by the notation

$$\pm \longrightarrow \mp.$$

"Under certain conditions it is also possible to obtain positive copies by an exposure in the camera and to print positives from positives and negatives from negatives. I call these copies *polarized* and this copying is represented by the notation

$$\pm \longrightarrow \pm.$$

"The blackening curve of a silver bromide gelatine plate, Fig. 1, shows an increase in blackening with increasing exposure during certain stages of the exposure; the curve extends away from the axis of abscissas and has a positive

[1] [Because the plate would be blackened uniformly over each section. W. D. B.]

sign. The curve for further exposure bends towards the axis of ordinates and has a negative sign.

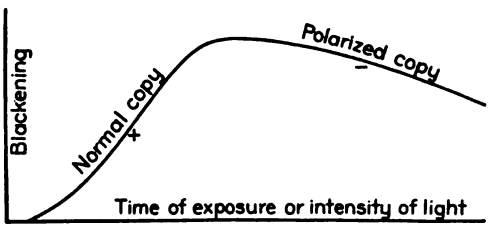

Fig. 1

"These curves are determined for constant intensity of light and varying time of exposure. The method given under *b* involves too much difficulty in determining the intensities of the lights. In so far as the reciprocity rule holds, the photographic effects are identical by the two methods. In practice there are large variations only at the beginning of the curve.[1]

"It is obvious that a positive blackening curve gives an unpolarized or normal copy by transmitted light while a negative blackening curve gives a polarized copy.

"Under solarization some people understand only the first reversal while others mean the periodicity of the blackening curve with increasing exposure, as discovered by Moser[2] and by Janssen,[3] including the three neutral points. The latter point of view is taken by H. W. Vogel[4] who includes still other periodicities, the existence of which has not yet been established definitely. On the other hand J. M. Eder[5] gives the following definition:

"'By solarization we mean the phenomenon that a silver bromide, silver iodide or silver chloride plate loses the power

[1] Michalke. Phot. Mittheilungen, 1890, 262; 1894, 53.

[2] Pogg. Ann., 58, 107 (1843).

[3] Comptes rendus, 90, 1447; 91, 199 (1880).

[4] Vogel's Handbuch der Photographie, 2, 78 (1894).

[5] Eder's Handbuch der Photographie, 1, II, 302 (1906); 2, 72 (1898); 3, 111 (1902).

to develop more or less completely after an exposure to light which is considerably longer than normal.

"'If a silver bromide plate is exposed to light by increasing stages, it acquires to a greater and greater extent the property of blackening in the developer. If the exposure is continued longer, the silver bromide plate gets into a state in which there is no increased blackening when developed. With a still longer exposure the photographic plate gradually loses the power of developing, the degree of blackening on development being less than with other silver bromide plates which have been exposed for a lesser length of time. This phenomenon is called solarization.'

"J. M. Eder[1] calls the periodicities 'additional repetitions of the solarization phenomena with prolonged exposure.'

"In other cases, as in the following, people mean by solarization *only* polarization.

"'If an emulsion plate has previously been exposed to a weak diffused light, a much shorter exposure will produce solarization than if the plate were intact.'[2]

"'Wood's experiments must therefore be interpreted to mean that there is a direct solarizing action with such intensities of light as will change the film when acting only for the forty-thousandth of a second.'[3]

"'Such a silver bromide emulsion which has changed in the dark gives distinct solarization phenomena when developed after an exposure to the solar spectrum.[4]

"'In addition there is another series of phenomena which resembles solarization in so far that a greater illumination causes a decrease in the power of the silver bromide to develop, whereby a much smaller amount of actinic energy is able to cause polarization during a second exposure.'

"Of these, we must distinguish two groups:

[1] Eder's Handbuch der Photographie, **2**, 78 (1898).

[2] Ibid., **2**, 74 (1898).

[3] Englisch. Eder's Jahrbuch der Photographie, **16**, 79 (1902).

[4] Eder. Sitzungsber. Akad. Wiss. Wien, **114**, II*a*, July (1905); Zeit. wiss. Photographie, **3**, 350 (1905).

"(1) The Herschel effect.

"(2) The Clayden effect.

"Still another phenomenon might be considered as a third group, the case in which a slight preliminary illumination serves to increase the sensitiveness of the plate. During the second exposure the power of the silver bromide to develop first increases and then decreases, as the time of exposure or the intensity of the light is increased. That we are dealing with a solarization is stated by J. M. Eder,[1] who says that 'if an emulsion plate has previously been exposed to a weak diffused light, a much shorter exposure will produce solarization than if the plate were intact.'

"With the Herschel and Clayden effect, it is quite different. When the second illumination exceeds a minimum value (induction limit), the power of the silver bromide to develop decreases *from the beginning*. Below the induction limit there is no change in the power to develop.

"I characterize as Herschel effect the phenomenon that some rays of light cancel the effect due to others.

"I characterize as Clayden effect the corresponding phenomenon which only occurs below a critical exposure.

"Claudet[2] ascribes the Herschel effect to a reverse reaction brought about by the second exposure which thus brings the plate back into its original state. 'La surface sensible ainsi regénérée peut servir à nouveau et recevoir une image ainsi bien que si elle n, avait subi aucune insolation.'

"R. W. Wood[3] does not distinguish between the Herschel and the Clayden effect. He says that the latter is the secondary illumination acting on a plate which has lost its sensitiveness in places as a result of the primary exposure.[4]

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[1] Eder's Handbuch der Photographie, 2, 74 (1898).

[2] Ann. Chim. Phys. (3), 22, 332 (1848).

[3] Astrophys. Jour., 17, 361 (1903).

[4] Eder's Jahrbuch der Photographie, 14, 532 (1900). One might just as well offer this explanation for the phenomenon of solarization of which Eder [Eder's Handbuch der Photographie, 2, 72 (1898)] has said that 'the continued action of the light apparently neutralizes the first effect.'

Later he gave another explanation.[1] L. Weber[2] gives an explanation which does not deal at all with the special cause of the phenomenon.

"Both with the Herschel effect and the Clayden effect it is just as permissible as in the case of solarization to assume that the developable silver compound, produced by the first exposure, changes into another which cannot be developed. E. Englisch[3] says that 'very probably we are dealing with solarization phenomena even though this assumption has been disputed very vigorously.' In the 'Ausführliches Handbuch der Photographie,' J. M. Eder[4] discusses the Clayden effect along with the solarization phenomena and therefore considers the two as related.

"Since no proof has been given that we are dealing here with phenomena which are really identical with solarization, it is improper to define solarization in such a way as to include these phenomena. Until this identity has been established, we must keep to the definition of solarization as given by J. M. Eder.

"By a solarized image I mean an image which consists of solarized silver bromide, *i. e.*, of silver bromide which shows a decrease in the power of development.

"When we have solarization phenomena we get a polarized copy. The two conceptions of solarization and polarization are interchangeable to the extent that we always mean a polarized copy when we speak of a solarized one. It is obvious that we can only say this when there is a simultaneous exposure to lights of different intensity. With a diffused illumination we can have solarization on a plate without being able to speak of polarization.

"We get polarization without solarization in copies where we have the phenomena of pseudo-solarization, in copies where the developed image acts as a reflector and not as an

[1] Wood: Astrophys. Jour., 17, 361 (1903).
[2] Camera Obscura, 1901, 515.
[3] Zeit. wiss. Photographie, 2, 40 (1904).
[4] Handbuch der Photographie, 1, II, 312 (1906); 3, 834 (1903).

absorber of light (collodion positives and Lippmann photochromes), etc.

"In addition to the case already cited in which there was no copy, we may probably get solarization without polarization in the Lippmann photochromes. I know of no case in which solarization has yet been shown in the so-called grainless emulsions. Lüppo-Cramer[1] has found that solarization occurred less readily the finer the grain; but this does not exclude the possibility of its occurrence. When photographing a continuous spectrum, for instance, solarization would cause a displacement of Zenker's leaves over a distance of $1/4\ \lambda$, which causes no change in the relative position of the ayers and therefore no change in the color.

"If one were to use this process in making a colorless photograph, for instance in reproducing a platinotype, the black would very probably appear white, while it is not certain that the white would be black since S. R. Cajal's[2] experiments indicate the existence of a plate-like structure in the white. In that case we should only get a partial solarization."

"As a result of experiments on fixing plates which have received a solarizing exposure, E. Englisch[3] comes to the conclusion that there are two images on a solarized plate. 'From the experiments described we may consider it proved that, beginning with an exposure depending on the intensity of the light, two different changes in the silver bromide gelatine go on simultaneously, a normal and a solarizing one.'[4] By this normal change it is not meant that the copy is necessarily normal.

"These experiments on fixing have been disputed by E. W. Buchner.[5] The difference in behavior is probably due to the degree of moisture in the gelatine.

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[1] Photographische Probleme, 146 (1907).
[2] Zeit. wiss. Photographie, 5, 222 (1907).
[3] Phys. Zeit., 2, 62 (1900).
[4] Archiv. wiss. Photographie, 2, 260 (1900).
[5] Eder's Jahrbuch der Photographie, 19, 385 (1905).

"J. M. Eder[1] considers it probable that in the case of solarization we have two images, one on top of the other, which differ in their chemical composition. He calls the solarized image positive, meaning polarized.

"Lüppo-Cramer[2] points out that there is a specific difference between the free surface of a polarized plate and the deeper layers, quite regardless of whether the glass side or the emulsion side had been exposed to the light.

"With increasing time of exposure or intensity of light, the power of the silver bromide to develop extends further down, finally to such an extent that the reduction reaches to the glass if the plate be developed long enough. The microscopical preparations of W. Scheffer[3] show this. If solarization occurs, it takes place just at what seems to be the most sensitive layer,[4] at the free surface. The power to develop begins to fail here first and the change to which this is due gradually penetrates deeper with increasing length of exposure or intensity of light. We get finally a form of image * * * from which we see at once that *the solarized image is a normal copy and a surface image.* The blackening curve of the solarized image, is therefore positive in direction.

"Under this image there is a polarized copy.....and from this to the glass there is a fogged layer, the blackness of which depends on the thickness of the poured film.[5]

"*In the case of solarization we nevertheless see a polarized copy because the normal copy is less black than the polarized one.* This however masks the contrasts and obscures the details more or less."

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[1] Zeit. wiss. Photographie, 3, 340 (1905).

[2] Phot. Correspondenz, 1903, 494.

[3] Eder's Jahrbuch der Photographie, 21, 31 (1907).

[4] Due to the surface tension rather than to the difference in the light-absorption in the films, which latter cannot be noticed in the case of Röntgen rays, for instance, especially if these are very hard.

[5] The strip of fog is of course dependent on the thickness of the poured film only in case the development has been carried far enough. When the development is not pushed far enough, the reduction does not extend to the glass.

IV. Fog and Solarization

"The fog on normal copies, resulting from too long exposure or development, can be removed with Farmer's reducer;[1] but this cannot be done with copies polarized by solarization. W. Scheffer[2] found that Farmer's reducer acted from plane to plane always parallel with the free surface where the action began. We must therefore assume that the reducing action affects first the solarized image, then the polarized copy and lastly the fogged layer in contact with the glass, so that it is impossible to remove the fog in this way without at the same time attacking the image. Changing the emulsion to another plate and letting Farmer's reducer act on the back of the film would help matters.

"A similar state of things prevails in regard to fog on silver bromide gelatine plates treated with potassium bichromate.

"Except with very thin emulsions and very strong lights, irregularities in the thickness of the emulsion film are of no importance for normal copies because we have to deal with a surface image. In the case of solarization these irregularities may be very disturbing through differences of blackness both in the fog and in the picture itself if the film is a thin one. This gives a simple method of checking the uniformity of the pouring in the case of thick emulsions."

V. Theory of Retarded Development of Solarized Plates

"Up to now it has always been assumed that the development affected the appearance of solarization. The reason for this is to be ascribed to the confusion in the conception of solarization and polarization. The following belief is held pretty generally.

"The stronger the developer and the longer one develops, the more marked is the polarization. By regulating the development one can prevent or cause the appearance of solarization.[3]

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[1] Eder's Handbuch der Photographie, 3, 115 (1902).
[2] Ibid., 21, 26 (1907).
[3] Ibid., 3, 114 (1902).

"By decreasing or neutralizing the alkali content of the developer, solarization is prevented.[1] The same result is obtained by adding potassium bromide, as stated by J. M. Eder.[2]

"In all these cases the rate of reaction of the developer is decreased. A normal copy appears first which changes to a polarized one when the development is prolonged. That this is the real explanation and that the presence or absence of reagents in the developer has nothing to do with it was proved by me when I showed that exactly the same series of phenomena took place when I used an ordinary developer (Rodinal 1 : 10) but worked at a low temperature.

"J. Precht[3] has put forward the theory that polarization is a development phenomenon which has nothing to do with any change in the constitution of the latent image of silver bromide caused by light. He has not been able to maintain this point of view against the criticisms of J. M. Eder.[4]

"If a plate which has received a solarizing exposure is given a retarded development so that only a normal copy appears and the surface is then examined at an acute angle in reflected light, we notice at once that the distribution of the developed silver bromide in the upper layer does not agree with that of the normal copy as given in Fig. 3.[5] The blacker places seem more shiny than the others.

"Lüppo-Cramer[6] has called attention to the polished look of solarized surfaces. In this case, however, the less black portions are more shiny than the blacker ones,[7] which is just the reverse of what is true for the normal copy of the solarized image obtained by delayed development. On

[1] Eder's Jahrbuch der Photographie, 3, 827 (1903).

[2] Theorie und Praxis der Photographie mit Bromsilber-Gelatine, 247 (1883).

[3] Phys. Zeit., 3, 426 (1902).

[4] Phot. Correspondenz, 1902, 570.

[5] [Not reproduced in this article.]

[6] Photographische Probleme, 142 (1907).

[7] The differences are much less than with the normal copy under ordinary conditions. In fact, the plate very soon shows a polish over the whole surface.

prolonged development there is therefore no change in the surface, from which it follows that the reversal of the image is not a surface phenomenon but takes place in a lower layer.

"The blackening at any arbitrarily selected spot cannot decrease when the development is prolonged but must increase. The reversal of the copy is therefore due to the fact that the less black portions on further development increase in blackness more rapidly than those portions which were previously the blacker. It follows necessarily from this, that for a moment there is a complete disappearance of the image, which is actually what happens.

"The inversion of the increase in blackening is to be ascribed to the presence in the deeper layers of more or less of a silver bromide which develops more rapidly than that at the surface. The further assumption is made that there is less of this silver bromide under the blacker places of the normal copy.

"Starting with these assumptions we deduce the same form of image for the polarized image in solarization that was given in Fig. 6.[1] *The normal copy produced by retarded development is therefore the solarized image*, which is like a very soft picture in showing only slight differences of blackness in consequence of the developability of the silver bromide being less or even zero.

"*A change of the solarization, i. e., of the substance of the solarized latent image cannot be accomplished by retarded development.*

"J. Precht's theory of development as the cause of solarization is therefore in complete contradiction with this theory of retarded development in the case of solarization.

"In the surface shine we have a means of checking up the solarization and of telling whether this or that reagent reacts only with the substance of the latent image or whether it merely hardens the gelatine for instance and thus produces a retarded development. In this way I was able to prove

[1] [Not reproduced in this article.]

that Eder's[1] chromic acid solution and the ammonium persulphate solution of K. Schaum and W. Braun[2] both harden the gelatine and also react with the substance of the latent image in the case of solarization, whereby this substance is converted back into that of the ordinary, latent image.

"Still another remarkable phenomenon is to be noticed. A normally exposed plate shows the first development[3] on the surface at the places where the intensity of light has been the highest. The same thing is true of those portions which have been exposed the longest to light of constant intensity. An over-exposure or an under-exposure does not change this in the least.

"With prolonged development the reduction of the silver bromide in the lower layer goes on fastest in those portions where the illumination has been most intense. What holds for the surface, therefore holds for all the deeper layers.

"If the most intense illumination causes solarization and thus prevents the silver bromide grains at the surface from developing, this first development cannot be recognized. The appearance of the normal copy with retarded development proves however that the most rapid increase in the reduction of the lower layers still remains at the portions which have received the most intense illumination.

"This proves again the impossibility of the hardening of the gelatine by free bromine having anything to do with the occurrence of solarization in silver bromide gelatine.[4]

"This difference in the rate of propagation of the development in the deeper layers may cause the normal copy

[1] Eder's Handbuch der Photographie, **3**, 828 (1903).

[2] Phot. Mittheilungen, **1902**, 224.

[3] Sheppard and Mees [Zeit. wiss. Photographie, **3**, 356 (1905)] say that the development begins at the *grains* which have received the most intense illumination. This is not quite right. Owing to the differences in the degree of ripening of the silver bromide in one and the same emulsion, with the same illumination those grains are first developed which are in the highest stage of ripening. It is better therefore to say that the portions receiving the most intense illumination develop first.

[4] It is assumed in the theory of tanning as modified and defended by E. Englisch.

by retarded development to contain both the solarized image. and also a part of the unsolarized silver bromide, *i. e.*, of that which later would form the solarized image."

VI. The Sabatier Polarization

"If one lets light strike the plate during the development, three different phenomena may occur:

"(1) If the light is weak, the plate shows an increased developability.

"(2) With a stronger light the image disappears to a certain extent and we get a rather thin, partially fogged plate, with a partly normal and a partly polarized copy which develops extraordinarily slowly.

"(3) With a very strong light we get a polarized copy.

"Under these circumstances we seem to get a change in the power of the silver bromide to develop which corresponds to the changes on continuous exposure.

"The polarization resulting from the action of light during the development is called by me the Sabatier polarization.

"J. M. Eder[1] describes this phenomenon in his standard work as follows:

"'Sabatier observed that a negative image on a wet collodion plate changed into a positive if the plate were exposed suddenly to daylight, during the development. The negative at once stopped developing, reversed and became a complete positive in less than a minute. De la Blanchère made the same observation, as did also Rutherford and Seely.

"'In the session of the American Society on January 9, 1850, Seely gave a very satisfactory explanation which made the whole phenomenon intelligible. The development at first is superficial and takes place only there where the light has caused a change. On the illuminated portions there forms a thin film of metallic silver which is partially opaque. This film of silver acts as a protection when the plate is exposed to diffused daylight, while the other portions of the

[1] Eder's Handbuch der Photographie, 2, 82 (1898).

plate are free to be acted on by the light. Since this action is a stronger one than the first, the development takes place where the diffused daylight caused a change, *i. e.*, in the shadows.

"'H. W. Vogel gives a similar explanation, namely that the light coming into the dark room affects the uncovered silver bromide very much, while that which is covered with a precipitate of silver is protected by it and is not attacked. The result is that there is a very energetic development in the shadows which of course causes a reversal of the image in case the light in the dark room is sufficiently intense and in case the previous development has not gone too far.'

"F. E. Nipher[1] describes the same process and E. Englisch[2] remarked in connection with this that 'Nipher has shown that the reversal only takes place well when the source of light for the after-illumination is sufficiently intense. That is his lasting service.' From the preceding paragraphs it appears clearly that one can not credit even this result to Nipher for H. W. Vogel had already pointed it out in 1870.

"V. Schumann stated that silver bromide gelatine plates, containing cyanine, polarized strongly if the plate were exposed for a few minutes during the development to a powerful red or yellow light.

"From the experiments which I have made, it appears that a strong illumination, after the plate has been pretty thoroughly developed and shows its strongest contrasts and its wealth of detail, gives results which are difficult to control.

"The best results are obtained if the plate is developed until the details begin to appear by reflected light in the dark room and if the plate is then exposed to direct daylight. That there was polarization by transmitted light could be determined only after the plate was fixed.

"Before fixing, the plate by reflected light shows the image as a normal copy, just as a plate does which has been developed after receiving a solarizing exposure. When the

[1] Trans. Acad. Sci., St. Louis, **10**, 151, 210 (1900); **11**, 51 (1901).

[2] Eder's Jahrbuch der Photographie, **16**, 80 (1902).

plate is exposed to daylight, the normal copy increases a little at the points where the blackening is least; but then goes no further, at least so far as one can see.

"This phenomenon shows that the explanation given by Seely and by H. W. Vogel does not account for all the facts connected with this polarization.

"In order to find out how far the copying action during the polarization depends on the already developed image, I followed the advice of P. H. Eykman and made the secondary exposure from the glass side.

"The exposed plate was developed for a short time. Soon after the appearance of the image, the plate was wrapped in a piece of opaque black paper which was pressed smoothly against the emulsion to avoid bubbles, which would affect the later development. The glass side of the plate was then exposed to direct daylight. Since the amount of developer absorbed by the paper was small and since the temperature was below normal, the plate was brought back into the dark room and placed again in the developer in order to hurry things up, care being taken to prevent any light reaching the front of the plate. When the plate was fixed, the copy was found to be polarized.

"From this it follows that any copying effect of the developed image plays at most a very subordinate part in causing polarization.

"The polarization can only be due to the developed image losing its power to develop further, while the silver bromide beneath it acquires an increased power of developing; or to a slight increase in the blackening of the normal image accompanied by a greater blackening in the silver bromide underneath. We therefore get two images, one superposed on the other. Above there is a normal copy with only a slight blackening, while underneath there is a polarized copy which is much blacker, thus agreeing with the polarized copy resulting from solarization.

VII. The Partial Disappearance of the Image Due to a Weaker Illumination during Development

"By a weaker illumination R. Lyle[1] obtained the results described under VI, 2. The partial disappearance of the image gives the plate apparently the appearance of a film which has reached a neutral point. Lyle believed that this was the first zero state of Janssen's periodicities. My experiments prove that the agreement does not go beyond the fact that no image is to be seen. The plate shows a slight blackening in its apparently neutral state while the first zero state is characterized by the occurrence of the maximum blackening. The reason for the disappearance of the image is therefore not due to this. By transmitted light the plate shows polarization at the places where the first illumination was the weakest and not where it was strongest. These latter portions are copied normally. Between the two we get the partial disappearance of the image.

"The time of the weaker, secondary exposure is of course of overwhelming influence on the question whether the relative induction limit of a deeper layer is or is not reached. At the thinner portions of the image the power of the adjacent deeper layers to develop will increase more rapidly than at the thicker portions because the adjacent layers are nearer the surface in this case and therefore have a lower relative induction limit. In this way the light will be weakened more by those portions of the image having a greater blackening than by those with a lesser blackening. Two causes therefore work together to minimize the extreme contrasts of the image.

"Where the image shows greater differences in the degree of blackening, we see that the plate polarizes first at the thinnest portions which causes the bringing out of the image by development to be decreased or even prevented. In this case we also get the occurrence of two opposing images of which the lower is the blacker.

[1] Phot. Centralblatt, 1902, 146.

"At the places where the blackening is the greatest, the increase in the power to develop is so slight that the polarization is negligible in comparison with that at the other places.

"Between these two states there must be a change from the normal to the polarized, *i. e.*, there must be a neutral state which begins at the thinnest portions of the image and encroaches on the thicker portions with increasing time of development and of exposure."

VIII. Explanation of the Sabatier Polarization by Solarization

"The agreement between the Sabatier polarization and the phenomenon of solarization is much clearer when one reflects that the polarization is more marked the more powerful the primary illumination. Conversely, if we first give the plate a strong illumination in diffused light and then a powerful exposure for the purpose of forming an image, we get a polarized copy. This is the so-called zero plate of F. E. Nipher, on which R. Neuhauss[1] says that he made the earlier experiments.

"Since the copying effect of the developed image can be left entirely out of account, the same phenomenon must also occur if the secondary, diffused illumination takes place *before* the plate is laid in the developer. This is actually the case.

"From these phenomena and from our conception of the form of the image we may conclude for the moment that the Sabatier polarization is a solarization phenomenon which merely appears in another form. The only facts against this view are the phenomena described under VII.

IX. The Clayden Effect

"In 1899 Clayden[2] observed, when photographing lightning, that a number of the ramifications of the bright flash of lightning appear polarized (dark lightning). This could

[1] Phot. Rundschau, 1900, 254.

[2] Eder's Jahrbuch der Photographie, 15, 610 (1901).

not be accounted for on the assumption of solarization due to excessive over-exposure.

"R. W. Wood[1] succeeded in obtaining the same phenomena by means of powerful electric discharges when a small diaphragm was used and the plate was afterwards exposed for a short time to diffused light. If the first exposure was longer than 1/50000 second a normal copy was obtained, quite in accordance with Clayden's photographs of lightning where the main flash remained entirely normal owing to the longer duration of the light. At first it was believed that this phenomenon was due to a special property of silver bromide, that a certain critical exposure of very brief duration (about 1/50000 second) caused it to lose its sensitiveness to a second illumination. This explanation could not be maintained after R. W. Wood and L. Radke, at about the same time (the former by new experiments), had shown that this critical exposure depended on the ratio of the two exposures.

"R. W. Wood[2] discovered the variation with varying intensity of the light. The more intense the light of the electrical discharge, the greater must be the intensity of the after-illumination.

"L. Radke[3] discovered that the critical exposure varied with the time of exposure. 'I exposed a burning candle, against a black background, five minutes side by side on the same plate for 5, 3.5, 1, 0.5 and 0.01 seconds and then exposed the plate for two seconds to the light of a burning match. When the plate was developed, it appeared that the after-exposure had been sufficient to reverse the whole light effect of the three shorter exposures and the halo as well as the upper edge of the flame in the case of the candles which had been exposed 3.5 and 5 seconds, while the parts which had received a stronger illumination were entirely unchanged. The experiment shows that the first exposure does not need to be so long as was stated by Wood, since an after-illumina-

[1] Nature, **61**, 104 (1899).
[2] Astrophys. Jour., **17**, 361 (1903).
[3] Phot. Mittheilungen, **1903**, 61.

tion of two seconds was enough to reverse an exposure of one second. From the instance just cited, we conclude that the time of the after-illumination stands in some relation to the first action of the light.'

"There are chemical reactions taking place very slowly in silver bromide gelatine plates which bring about a state corresponding exactly to that produced by light. J. M. Eder[1] pointed out that we may even get solarization phenomena. The following shows that we may also get the Clayden effect in this way.

"Some time ago one of my friends showed me a couple of pictures taken on Eastman films and I recognized in them another form of the Clayden effect. The films had been exposed in the usual way but had remained for about three years in the camera without any care except precaution against the entrance of light. The exposure to diffused light was here replaced by a chemical decomposition of the silver bromide acting in the same way, due to vapors from the celluloid which diffused into the silver bromide."

X. The Herschel Effect

"In 1839 J. Herschel observed that the less refrangible rays of the spectrum could counteract the action of the more refrangible rays. Claudet[2] confirmed this later and showed that the plate was afterwards 'in a condition to give a new image. He drew the conclusion that the secondary exposure had brought the plate back into its original state.

"Warnerke[3] described the following experiment. He wrote on a plate with a stick, using pressure but not damaging the gelatine. He exposed the plate and afterwards wrote again on the plate in the same way but in another place. When the plate was developed, what was written before the exposure appeared light on a dark ground while what was written after the exposure could scarcely be seen and was a

[1] Eder's Handbuch der Photographie, 1, II, 296 (1906).
[2] Ann. Chim. Phys. (3), 22, 332 (1848).
[3] Phot. Archiv., 1881, 120.

trifle darker than the background. Warnerke draws the same faulty conclusion as the others, that pressure decreases the sensitiveness of silver bromide. He overlooks entirely the fact that this pressure formed silver bromide which could be developed.

"H. W. Vogel[1] says that a silver bromide gelatine plate, when bathed in a Judson's blue solution and exposed to the spectrum, showed polarization first in the red and much later in the green.

"W. Abney[2] made a series of experiments in which he gave the plate a preliminary exposure to diffused light, then bathed the plate in a solution of an oxidizing substance and afterwards exposed it to the light of the spectrum. A change in the color-sensitiveness was observed, but Abney considered the phenomena as solarization.

"A series of admirable experiments were made by P. Villard with the Röntgen rays soon after their discovery. He ascribed the results to the antagonistic effect of the light. P. Villard[3] showed that the phenomenon did not occur equally well with all plates. The Jougla plate with a green label was the best of those he tried. When these plates were exposed first to Röntgen rays and afterwards to ordinary light, polarized images were obtained. The reverse order of illumination—when the plates were exposed first to ordinary light and then to the Röntgen rays—caused no polarization. He observed also that the polarization was most marked when red light acted on the plates, and he was thus able to make plates sensitive for infra-red rays. The plate is sensitive for the whole spectrum but shows a minimum in the green. 'On peut dire cependant que l'émulsion est devenue réellement panchromatique.' He also used a weak light in the after-exposure.

"R. Luther and W. A. Uschkoff[4] confirmed the results

[1] Vogel's: Handbuch der Photographie, 1, 221 (1890).
[2] Ibid., 1, 224 (1890).
[3] Société d'Encouragement pour l'Industrie nationale, Nov. (1899).
[4] Phys. Zeit., 4, 866 (1903).

of Villard to the extent that they also showed that a secondary exposure to Röntgen rays gave an effect which was superposed on that of the primary exposure, while a decrease in the photographic effect is obtained when a primary exposure to Röntgen rays is followed by an exposure to daylight.

"J. Sterry[1] noticed that certain forms of chemical fog could be removed by an exposure to a weak light. This is suitable for silver chloride gelatine plates which are to be developed.

"Though considered by E. Englisch[2] to be a new discovery, the periodicities in the curve of blackening of a silver bromide gelatine plate are merely a Herschel effect, the variations being due to the intermittent illumination. People have disputed Englisch's results and V. Vojtech[3] ascribed them to experimental error. The truth of the matter is that Englisch's opponents did not get the Herschel effect which only occurs occasionally and which depends on a number of factors[4] other than those mentioned.

"R. W. Wood[5] describes a number of these experiments again under the Clayden effect, thus postulating the identity of the two phenomena. If the intensity of the light is too great during the after-illumination, there is no polarization. There is no polarization when Röntgen rays are used for the secondary illumination. Wood also confirmed the change in color-sensitiveness which appears in the secondary illumination and discovered the new fact that the simultaneous action of Röntgen rays and the light of a lamp gave a photographic effect which was less than the sum of the single effects (Wood effects).

"This can also be seen in a Röntgen ray photograph placed at my disposal by P. H. Eykman. The plate was ex-

[1] Phot. Jour., 43, 290 (1903).
[2] Phys. Zeit., 3, 1 (1901).
[3] Phot. Correspondenz, 1904, 398.
[4] This will be discussed more in detail later.
[5] Astrophys. Jour., 17, 361 (1903).

posed to Röntgen rays with a so-called intensifying screen (calcium tungstate screen) and was laid aside for a while before being developed. The calcium tungstate gave an after-luminescence[1] which caused a further exposure of the plate. A piece of bone, a thinner and a thicker piece of insulated copper wire were being photographed. The negative is reproduced in Fig. 10.[2] The portions of the plate covered by the thin copper wire show a development of the silver bromide which is almost as strong as that of the background where the Röntgen rays and the luminescence from the calcium tungstate have both acted the most intensely. A narrow strip along the edge shows how far the calcium tungstate screen covered the plate. In this strip the Röntgen rays alone have acted and here the portions covered by the thin copper wire show no sign of development. The amount of light from the Röntgen rays passing through the thin copper wire was therefore below the induction limit.

"The development cannot be due to irradiation from the calcium tungstate because then it would be noticed with the thick copper wire and at the edge of the screen. The Röntgen rays must therefore actually have acted at these places in such a way that the screen gave out light and reduced the silver bromide even though the illumination by the Röntgen rays was below the induction limit. This may be due to the great absorption of the energy of the Röntgen rays by the copper wire or, though less probably, to the action discovered by B Walter,[3] of the secondary rays of the phosphorescing part of the glass wall of the Röntgen tube. This does not affect the photographic result.

"It is therefore clear that the weak luminescence of the calcium tungstate screen has here produced a greater photographic effect than on the intensely illuminated portions where it and the Röntgen rays both acted.

"P. H. Eykman showed me also a plate in which the

[1] Fortschritte auf dem Gebiete der Röntgenstrahlen, 4, 180 (1901).

[2] [Not reproduced in this article.]

[3] Fortschritte auf dem Gebiete der Röngtenstrahlen, 4, 241 (1901).

screen was first acted on by the Röntgen rays and then brought in contact with an unexposed plate. The result was a very thin picture. It appears therefore that the screen produces the strongest effect immediately after the transformation of the energy of the Röntgen rays takes place. If one could eliminate the action of the Röntgen rays when taking a picture with them in the presence of a calcium tungstate screen, it would be possible to obtain an image with a much shorter exposure than is now the case. So far it has not proved possible to do this."

XI. The Identity of the Clayden and the Herschel Effects

".....The difference [between the Clayden and the Herschel effect] is merely that in the Clayden effect the critical illumination is exceeded in certain portions of the plate while this is not the case in the Herschel effect. There is a gradual but no essential difference.

"In the study of the Herschel effect, people have hitherto paid attention chiefly to the nature of the light while in the study of the Clayden effect they have paid attention especially to the critical illumination.

"The very fact that the critical illumination has a variable and not an absolute value points to the impossibility of considering the Clayden effect as essentially different from the Herschel effect. R. W. Wood[1] treated the Herschel effect as a Clayden effect.

"A further agreement is to be found between the phenomena. Claudet[2] says that after the power to develop has been neutralized, *i. e.*, when the greatest transparency has been reached by the secondary exposure, the plate is again in a position to give a normal copy. We have the same thing with the Clayden effect when the critical illumination is exceeded.

"P. Villard[3] was able to show spectroscopically that

[1] Astrophys. Jour., **17**, 361 (1903).
[2] Ann. Chim. Phys. (3), **22**, 332 (1848).
[3] Société d'Encouragement pour l'Industrie nationale, Nov. (1899).

green light has the least effect in the secondary illumination. Also the possibility, to which I have referred, of replacing the first exposure by a chemical reduction producing analogous results, is realized in Sterry's discovery.

"We may therefore consider the Clayden effect and the Herschel effect as essentially identical phenomena, the former being a special case of the latter.

"To obtain the two phenomena it is however necessary that the primary illumination shall exceed the induction limit. When this is not the case, we get the well-known auto-sensitizing."

XII. The Behavior of the Herschel Effect with Much Longer Exposure

"Several cases of this are known to me. P. Villard shows an instance of this in one cut without discussing the matter. One-half of the plate was illuminated by Röntgen rays and later the whole plate was exposed to the spectrum in such a way that the spectrum fell both on the half of the plate which had been acted on by the Röntgen rays and also on the half of the plate which had not been exposed at all. On this latter half the plate showed solarization in the region of the blue while nothing of the sort was to be detected on the first half which appeared quite normal except for a decrease in the developing power of the silver bromide.

"W. Abney's[1] experiments are also nothing more than a Herschel effect with a very long exposure so that the result appears identical with solarization.

"A similar effect is to be seen . . . in a picture which P. H. Eykman very kindly placed at my disposal. It is a reproduction of the original picture and the contrasts have been increased very much by making two contact prints, first on a silver chlorbromide plate with development and then on collodion paper.

"The plate was taken out of the box and exposed to daylight. Next, it received a long exposure to Röntgen

[1] Vogel's Handbuch der Photographie, I,, 224 (1890).

rays, all other light being carefully excluded. The plate was then exposed again to daylight and developed. The copy proved to be polarized."

Trivelli discusses the theory of the latent image under twelve headings: (*a*) general sketch; (*b*) photochemical change of the silver subhalide; (*c*) the effect of the halogen involved on the photochemical decomposition of the silver halide; (*d*) the development; (*e*) the silver subhalides of the latent image. In this last section he criticizes the theories of Scheffer[1] and of Homolka[2] and then goes on as follows:[3]

"It appears[4] therefore that the silver subhalide nucleus loses its characteristic of being a nucleus on further exposure and changes by another photochemical decomposition into another subhalide with a lesser halogen content, which does not act as a nucleus. We will call the first the α-silver subhalide and the second the β-silver subhalide.

"The re-appearance of the power to develop when the exposure is prolonged, the so-called second inversion of the solarization, could be accounted for either by assuming still another silver subhalide, the γ one, or, since the third reversal is not definitely established, by assuming the existence of metallic silver nuclei, or by a combination of these assumptions. We must also keep in mind that it is by no means impossible that before we get to the α-silver subhalide there may be one or more halogen-richer subhalides which cannot act as nuclei, for a preliminary exposure of the plate below the induction limit brings about some photochemical decomposition causing an auto-sensitizing.[5] Consequently the induction limit so-called is not identical with the photochemical induction.[6] It would be just as wrong to deduce from the preceding that the α- or the β-silver subhalide does not

[1] Phot. Correspondenz, 1907, 487.

[2] Ibid., 1907, 163.

[3] Trivelli: Zeit. wiss. Photographie, 6, 278 (1908).

[4] From the behavior of a solarized plate which is first fixed and then developed.

[5] See J. M. Eder: Sitzungsber. Akad. Wiss. Wien. 1908, IIa, 1407 (1899).

[6] Pogg. Ann., 100, 481 (1851).

consist of more than one silver subhalide.[1] From all this it appears that *it is not permissible to identify light-sensitiveness with power to develop*, though this is usually done."

(f) The theory of the Herschel or Clayden effect

"When discussing the Herschel and Clayden effects it was pointed out that people have generally tried to explain these phenomena by the assumption that the illuminated silver halide is brought back to its original condition by the second exposure or that it loses its sensitiveness (identification of light-sensitiveness with power to develop). J. M. Eder[2] says in regard to this that 'it is difficult to reconcile this observation with the present theories of the formation of photographic images.'

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[1] This differs somewhat from J. M. Eder's point of view [Eder's Handbuch der Photographie, 1 II, 310 (1906)]. "Although it is very doubtful whether the solarization image consists of an oxybromide, it is nevertheless probable that the substance of the normal latent image has a different composition from that of the solarized image. It is possible that in the normal latent image we have a larger complex of less decomposed silver bromide molecules as photobromide, while in the solarized image the splitting has gone further (the substance of the latent image might, for instance, be Ag_mBr_{m-1} and that of the solarized image Ag_nBr_{n-1} where $m > n$) and has produced a silver subbromide which is more stable towards the developing solution and which also is chemically different in other ways.

"This view agrees with that of Ostwald's rule of stages, according to which in all chemical reactions those products are formed first which are the more *labile* under the conditions of the experiment. According to this natural law which gives us a general point of view in working out a reaction process, it is not improbable that the first photochemical decomposition product of silver bromide (*i. e.*, the normal latent image) is more labile, more readily reduced (more ready to react) than the next decomposition product, namely the more difficultly reducible substance of the solarized image."

I assume only the existence of the β-silver subhalide (Ag_nHal_{n-1}) *without* the power of forming a nucleus and of the α-silver subhalide (Ag_nHal_{n-a} where $a < b$) *with* the power of forming a nucleus. These show essential differences (but both remain unreduced by the developer), and the relative quantities resulting from different illuminations give gradual differences as will be shown later. J. M. Eder, on the other hand, assumes the existence of two subhalides with gradual differences, the second being formed only in the case of solarization.

[2] Eder's Handbuch der Photographie, 1 II, 296 (1906).

"R. W. Wood[1] later attempted an explanation on the basis of J. C. Bose's[2] mechanical strain theory; but this has been criticized by E. Englisch[3] as unsatisfactory. Englisch[4] himself assumes, as does H. W. Vogel,[5] that the phenomenon originally observed by J. Herschel is a case of solarization. He[6] considers the Clayden effect as possibly dependent on the periodicities which he, Englisch, thinks he was the first to discover.

"L. Weber[7] defended the point of view that silver bromide shows first a decrease and then an increase in sensitiveness to light (identification of light-sensitiveness with power to develop), only the decrease in light-sensitiveness taking place when the exposure is very short. This is not tenable for we know that the preliminary exposure is capable of producing an image which can be developed and that the phenomenon in question has never been observed in the case of a continuously prolonged exposure.

"W. Abney's bromide theory need not be considered because he believed that he was dealing with solarization and that has already been considered.

"To obtain the Herschel effect it is necessary that the preliminary exposure exceed the induction limit of the plate. The α-silver subhalide must therefore be formed.

"We cannot assume that a reverse reaction takes place between the halogen and the α-silver subhalide because with a very prolonged exposure the Herschel effect passes into solarization for which we have already established the formation of the β-silver subhalide with no power to form nuclei. Also the experiments of Abney show that the phenomenon is helped by an absorption [?] of halogen. The secondary exposure therefore acts in such a way that the

[1] Astrophys. Jour., **17**, 361 (1903).
[2] Proc. Roy. Soc., **70**, 185 (1902).
[3] Zeit. wiss. Photographie, **2**, 140 (1904).
[4] Archiv. wiss. Photographie, **1900**, 11.
[5] Vogel's Handbuch der Photographie, **1**, 225 (1890).
[6] Eder's Jahrbuch der Photographie, **16**, 79 (1902).
[7] Camera Obscura, **1901**, 515.

α-silver subhalide, produced photochemically by the first exposure, is reduced to the β-silver subhalide faster than α-silver subhalide is formed again. It may thus happen that the α-silver subhalide is completely decomposed photochemically before the silver halide can furnish any more. . . . The photochemical induction of the α-silver subhalide therefore lies below the induction limit of the silver halide. *In the α-silver subhalide we therefore have a substance of greater sensitiveness to light than the silver halide.*

"If the secondary illumination increases the amount of α-silver subhalide, we get a normal copy. The critical exposure is therefore the one in which the secondary exposure produces the *same amount* of silver subhalide as was present after the preliminary exposure.[1] We should get therefore the best gradation of the polarized copy with the Herschel effect when the secondary exposure is made with weak intensities of light, which is what all the experiments have demonstrated.

"Luggin's modified law is to the effect that with a light of definite intensity the decomposition of the silver bromide will take place only up to a point of equilibrium if there is no removal of the halogen which is set free. This removal of halogen may take place through diffusion or through the action of chemical sensitizers and has an overwhelming effect on the occurrence of the Herschel effect. The experiments succeed well with an emulsion which absorbs the halogen directly or better still if there is a long interval between the preliminary and the secondary exposure so that the halogen has no chance to diffuse out. It is even simpler to treat the plate after the preliminary exposure with a substance

[1] It appears to me therefore desirable to distinguish two states *below* the critical illumination: *a complete polarization*, which occurs with a secondary exposure below the induction limit of the silver halide; and *an incomplete solarization* when the secondary exposure exceeds the induction limit of the silver halide. If the bromine set free photochemically is not entirely absorbed or removed by diffusion, a small amount of the α-silver subhalide may be decomposed by the secondary exposure, in which case we get *an incomplete Herschel effect*, just as was found by Englisch and by Luther and Uschkoff.

which absorbs halogen as W. Abney did[1] and we may assume that the Judson's blue, which H. W. Vogel used,[2] probably acts in a similar way.

"For the same reason we get the Herschel effect very well when the direct decomposition of the silver halide is caused by reducing agents which act slowly, as in Sterry's experiments and in the case of the Eastman film (p. 309), where the halogen is taken up at once.

"Villard's observation that all emulsions are not equally suitable is now quite intelligible, because the different emulsions contain different kinds and amounts of chemical sensitizers.

"The reason for the phenomena obtained with intermittent exposure is now somewhat clearer. W. Abney,[3] K. Schwarzschild,[4] and others have observed that the effect of the developer on silver bromide gelatine is always a little less for an intermittent exposure than for the same total exposure when made continuously. Many beginners have noticed the same thing when they made two different exposures on the same plate. In such a case it is easy to note that one does not get a summation of the two pictures. Instead, one predominates in one place and the other perhaps in another.

"According to K. Schwarzschild the result of an intermittent illumination depends largely on the ratio of the time between the exposures to the time of the exposures. The development is less the longer the time between the exposures.

"The total amount of halogen formed depends on the length of the several exposures. The longer the period between the exposures, the more chance there is for the halogen to escape by diffusion or for it to be absorbed by a chemical sensitizer and therefore the next exposure will prefera-

[1] [There seems to be a confusion in regard to the facts. Abney obtained a polarized copy when he added oxidizing agents and not when he added bromine absorbers. W. D. B.].

[2] Vogel's Handbuch der Photographie, 1, 221 (1890).

[3] Photography, 1893, 682.

[4] Phot. Correspondenz, 1899, 171.

bly convert photochemically the α-silver subhalide into β-silver subhalide and halogen where the effect of development will be less than the sum of the single effects, quite apart from the photochemical induction which has to be overcome again.

"The difference between the silver halide and the α-silver subhalide in respect to sensitiveness to light appears from the experiments in question to depend very markedly on the nature of the rays constituting the secondary exposure. The Herschel effect will be more striking, the less sensitive the silver halide is to a given color and the more sensitive the α-silver subhalide is for the same color. The lesser this difference, the quicker will new α-silver subhalide nuclei be formed from the silver halide.[1] While there will be perceptible polarization even in this case, the minimum power of developing will be reached quickly. This is of course also dependent on the amount of α-silver subhalide present, in other words, on the length of the primary exposure. A complete destruction of the power to develop need not occur.

"The change in color-sensitiveness with the Herschel effect is thus to be ascribed to the different color-sensitiveness of the silver subhalide. No single one of the other existing theories of the latent image accounts for this phenomenon so simply as does the subhalide theory. The subhalides are colored substances having an entirely different color from the silver halide and therefore having entirely different absorption spectra. There is therefore the possibility of an entirely different color-sensitiveness and the experiments of O. Wiener[2] show that this difference in color-sensitiveness actually occurs.

"P. Villard showed spectroscopically that the greatest difference between the induction limit of the silver halide and the photochemical induction of the α-subhalide is in the

[1] This photochemical decomposition probably takes place according to an exponential formula.

[2] Wiedemann's Ann., **55**, 225 (1895).

red, so that the α-silver subhalide is a substance sensitive to red. If one exposes a silver bromide gelatine to the action of a continuous spectrum, the power to develop will extend further from the blue into the red as the exposure increases. After development it appears that the density of the plate increases in the blue but that even with a prolonged exposure the density is but slight in the yellow, in the orange, and especially in the red. The reason why the density does not exceed a very low maximum is that the α-silver subhalide is much more sensitive to the red than is the silver halide, so that a state of equilibrium is soon reached in which just as much α-silver subhalide is destroyed as is formed.

"Some people consider the substance of the developable latent image as identical with Carey Lea's photohalide. How does this latter behave in red light?

"Carey Lea[1] exposed his pink photohalide to the action of a spectrum and found that 'in the red it remained unchanged' while it changed in all the other colors. *From this it follows that the subhalide nucleus of the latent image must be a different substance from Carey Lea's photohalide.*

"The action of the Röntgen rays is different from that of the other forms of light.[2] According to P. Villard, to R. Luther and W. A. Uschkoff, and to R. W. Wood these show no Herschel effect in secondary illumination. This cannot be due to a lack of sensitiveness of the α-silver subhalide to Röntgen rays. It is true that F. Hausmann[3] and others have reported that Röntgen rays do not produce solarization and therefore do not cause the formation of any β-silver sub-bromide.

"P. H. Eykmann,[4] however, and later, K. Schaum and W. Braun[5] have shown that solarization does occur with

[1] Am. Jour. Sci. (3), **33**, 363 (1887).

[2] Pressure also produces a different effect. I reserve the right to make more detailed communications in regard to the action of pressure on the α-silver subhalide.

[3] Fortschritte auf dem Gebiete der Röntgenstrahle, **5**, 89 (1901).

[4] Ibid., **5**, No. 4 (1902).

[5] Zeit. wiss. Photographie, **1**, 382 (1904).

Röntgen rays. The α-silver subhalide is therefore sensitive to Röntgen rays and the non-appearance of the Herschel effect is probably due to the fact that the value for the induction limit for silver halide with Röntgen rays is about the same or even less than the photochemical induction of the α-silver subhalide. In Röntgen ray photography therefore an intermittent exposure produces no photographic effect less than that of a continuous illumination. This is quite apart from the having to overcome the photochemical induction every time."

(g) The action of chemical sensitizers

"From Luggin's modified law it appears clearly that chemical sensitizers increase the photochemical decomposition of the silver halides by absorbing the halogen. They prevent *the reverse reaction.*

"Lüppo-Cramer[1] describes the following experiment, which confirms this. There is no trace of an increased sensitiveness to light when the photochemical decomposition of precipitated silver chloride takes place in presence of silver nitrate or of ammonia though these are both substances which absorb chlorine. On the other hand, in an emulsion, in which halogen does not escape rapidly when set free, chemical sensitizers are effective. From this it follows that the chemical sensitizers do not react with the silver halide.

"The serious variations from the rule of reciprocity in a silver bromide gelatine plate at very low intensities of light proves that gelatine is not a chemical sensitizer, a fact which has been established experimentally in another way by Lüppo-Cramer.[2]

"While the chemical sensitizers are very effective in printing processes, Lüppo-Cramer[3] has pointed out that they are of no value or may even be harmful in the case of silver halide emulsions which are to be developed. If one con-

[1] Phot. Correspondenz, 1901, 224.
[2] Photographische Probleme, 33, (1907).
[3] Phot. Correspondenz, 1903, 25.

siders that the α-silver subhalide nucleus is extremely sensitive to light and changes with loss of halogen into the β-silver subhalide which does not form a nucleus, it is clear that a chemical sensitizer which is too active would not increase the power of development.

"A number of chemical sensitizers are at the same time oxidizing agents. From the preceding it appears that oxidation changes the β-silver subhalide into the α-silver subhalide, thus destroying the solarization. This may be represented by the equation:

β-silver subhalide + oxygen = silver oxide + α-silver subhalide,

and the further oxidation by the equation:

α-silver subhalide + oxygen = silver oxide + silver halide.

"This reaction seems often to take place very slowly with the sub-bromide.

"Complications may also arise in that the chemical sensitizer may cause photochemical reduction on the one hand and on the other may change the β-silver subhalide when formed into the α-silver subhalide. In this case the chemical sensitizer has a beneficial effect on the development. This happens with a silver iodide collodion plate and silver nitrate which latter is a strong oxidizing agent[1] in the sunlight, so that it is questionable whether the so-called nullification of the solarization may not be an actual one and due to this."

(i) Theory of solarization

"It has been pointed out that, when we have solarization after a primary fixing and a secondary development, we may assume the existence of a silver halide which has not the property of forming nuclei for development; but this does not explain the phenomenon of solarization.

"For greater clearness, in the following lines we shall assume a photochemical decomposition and an immediate elimination of the halogen set free. Actually the real course of the changes is not as given below, because the different

[1] Carey Lea [Phot. Correspondenz, 1887, 346] and also Lüppo-Cramer showed that the silver photo-iodide is a very easily oxidizable substance.

plates behave differently, depending on the way they are made. Not only is the amount of the chemical sensitizer of importance but also the rate with which the sensitizer reacts with the halogen.

"If one exposes a photographic plate a long time, the silver halide will keep changing into the α-silver subhalide which acts as a nucleus for development. From the Herschel effect we know that this α-silver subhalide is itself a substance very sensitive to light so that we cannot assume that there is a continuous increase in nuclei. The α-silver subhalide changes rapidly into β-silver subhalide and halogen. In consequence there is a state of equilibrium at the surface of the silver halide grains, and the number of nuclei depends on the rate of formation and destruction.

"If the amount of the silver halide present in the surface of the grains decreases, the quantitative formation of the α-silver subhalide will also decrease. Since this latter has a higher light-sensitiveness, there will necessarily be a decrease in the total amount of the α-silver subhalide and consequently a decrease in the power of development; in other words, we shall have solarization.

"The phenomenon is therefore entirely dependent on the available surface of the grains (size of grains). In Lüppo-Cramer's[1] experimental investigations he calls attention very often to the fact that 'the size of the original silver bromide grains has a very important bearing on the formation of a solarized image.'

"The smaller the grain of the silver halide and consequently the greater the ratio of the silver halide in the surface to the total silver halide, the longer can the photochemical decomposition be prolonged without causing a decrease in the power to develop.[2]

[1] Photographische Probleme, 146 (1907).

[2] It is impossible to reconcile with these facts the theory of F. Kogelmann [Die Isolierung der Substanz des latenten photographischen Bildes, 1894] which postulates that in the case of solarization the light destroys also those molecules of silver bromide on the inside of the grain, while the change is chiefly on the surface of the grain when the exposure is normal.

"Of course this does not actually take place so rapidly. The plates of different makes contain different kinds and amounts of chemical sensitizers. Together with the differences in diffusion, this results in the plates of different makes beginning to solarize after very different exposures.

"The thiosulphate reaction brings out phenomena which are now explicable. The subhalides are decomposed by thiosulphate into silver and silver halide which latter changes finally to silver thiosulphate and goes into solution as a double [complex] salt. Instead of the α-silver subhalide nuclei and the β-silver subhalide, we have silver which also possesses the properties of nuclei as we see from the fact that plates can be developed after they have been fixed. If a strong solarizing exposure has been given, there is still solarization when the plate is first fixed and then developed, so that the reaction between the β-silver subhalide and thiosulphate must be one which takes place slowly just as was the case with the oxidation previously cited. If one is dealing with a highly sensitive plate having large grains, one therefore with a relatively small surface, or, in other words, with a small amount of β-silver subhalide, the reaction in the gelatine will take place faster than if there were a larger amount of β-silver subhalide in the same gelatine as would be the case with a fine-grained emulsion. The power of development will therefore show an increase (not to be confused with an acceleration), so that the solarization will be less, more, or completely checked, depending on the concentration of the thiosulphate solution and the time that it acts.

"This phenomenon was observed experimentally by Kogelmann,[1] Vidal,[2] and Englisch,[3] while Lüppo-Cramer[4] could not detect any solarization at all with a preliminary fixing in the case of highly-sensitive coarse-grained plates which take longer to fix than do the fine-grained plates.

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[1] Eder's Jahrbuch der Photographie, 9, 419 (1895).
[2] Bull. Soc. franç. Photographie, 1898, 583.
[3] Eder's Jahrbuch der Photographie, 15, 608; 16, 79 (1902); 18, 423 (1904).
[4] Photographische Probleme, 150 (1907).

"As was stated by Lüppo-Cramer,[1] the sulphocyanate prevents solarization in an entirely different manner."

(k) The Sabatier polarization

"In the Sabatier polarization the great decrease (nullification) in the development is not to be ascribed to a decrease in the number of nuclei because these have already fulfilled their function.[2] The decrease in the development can only be due to a diminished rate of development, due to a marked decrease in, perhaps to a total absence of, the supply of material to be developed. The theory of the so-called chemical development postulates that the silver subhalide is less soluble in the developer than the silver halide. For that reason the more rapidly dissolving silver halide may precipitate after the reduction on the nucleus which remains entirely unchanged. If the secondary exposure is intense enough, the substance to be developed will be surrounded completely by subhalide and the rate of development will therefore be decreased. This will take place even more rapidly in the developer because the developer is a halogen absorber.

"We are therefore dealing with a phenomenon which is really not a solarization though there is a strong resemblance between the two from a superficial point of view."

(m) Final conclusion

"From the preceding sections we can draw a few conclusions which are of the greatest importance in actual practice.

"Both in the α-silver subhalide and in the corresponding sub-iodide we have substances which are much more sensitive to light than the corresponding silver halide. If one could make emulsions in which these substances were present together with the silver halide which is necessary as the

[1] Photographische Probleme, 155 (1907).

[2] There is not a single reason for assuming that this reduced substance consists solely of α-silver subhalide, which is decomposed into β-silver subhalide by the secondary exposure and thus checks development.

substance to be developed, we should have plates which would be much more sensitive to light than the present ones. A chemical sensitizer would be in every respect desirable as a means of obtaining practical results. Such plates would follow the rule of reciprocity absolutely and would therefore give more exactly the relative light intensities of the object to be photographed, which would be of great value in astronomical photography, for instance, for determining the relative intensities of light of the stars by photochemical methods (photometry).

"The α-silver subhalide can be sensitized optically so that it may find a very extended applicability. We do not yet know accurately the color-sensitiveness of the α-silver subhalide in a pure state. The experiments that have been cited show only the *difference* between the sensitiveness to light of the silver halide and the α-silver subhalide. (It is very probable that the color of the α-silver subhalide is *green* because the polarization in the case of the Herschel effect begins in the red, and the green is the region of least sensitiveness.) The greater this difference the more favorable is the result. We should therefore expect the best results with unripe silver chloride plates containing α-silver subiodide and it is a question whether it may not be possible to ripen this latter.[1] The β-silver subhalide appears to be only slightly sensitive photochemically which is distinctly fortunate from a technical point of view."

XVI. The Form of the Image with the Clayden Effect

"In regard to the form of the image with the Clayden effect, we may refer for the most part to what has been said about the Herschel effect.

"It is clear that the normal copy after the critical exposure is again a surface image. If a large part of the silver halide present in the surface of the grain is already changed into α-silver subhalide and halogen, then the secondary ex-

[1] There are some experiments which seem to indicate that the silver subhalide does not ripen.

posure cannot form as much more α-silver subhalide as it would have done if the preliminary exposure had not taken place. We therefore get a lesser blackening in some portions than we would have had if the plate had not been exposed before.

"When the primary exposure is continued for a long time it may cause solarization because the supply of silver halide in the surface of the grains is not sufficient to form as many nuclei as were present before. In this case the Herschel effect becomes identical with solarization and the Clayden effect cannot be detected any more."

"From all that has been said, it appears that we may consider the Herschel effect or the Clayden effect as a special case of intermittent exposure. There are some experiments however which conflict with the theory which I have given. Thus in the paper already referred to, P. Villard reproduces a series of pictures illustrating the polarization of the image with different lengths of secondary exposures. From these we should naturally conclude that the silver halide shows an increased power of development before the α-silver subhalide begins to decompose. Villard's experiments show, however, that we are dealing with an incomplete Herschel effect, in other words, that the halogen set free has not been completely removed. The result of this is that, in the place where the α-silver subhalide has been formed by the primary exposure, the further decomposition caused by the secondary exposure is not as great as in those portions which did not receive a primary fixing."

The general conclusions to be drawn from the three papers on the problem of solarization may be summed up as follows, though it must be recognized that some of the conclusions are mutually exclusive and that the accuracy of most of them is a matter of opinion. The names in parentheses mean that these men vouch for the facts or have held the opinions cited but not necessarily that they are the discoverers:

1. A reversal of the photographic image may be obtained

with daguerreotype plates, with collodion plates, with gelatine plates, and with pure silver bromide. The reversal is therefore due primarily to a change in the silver salt which is independent of the nature of the material, such as gelatine or collodion, in which the silver salt may be embedded. The nature of the gelatine or collodion, however, has a marked effect on the readiness with which reversal takes place.

2. It is much easier to obtain a reversal with a gelatine plate than with a collodion plate and it is quite difficult to obtain a reversal with pure silver bromide. Reversals occur much more readily with a coarse-grained gelatine emulsion than with a fine-grained one.

3. A reversal of the photographic image may be obtained by a prolonged exposure; by the antagonistic action of light of different colors (Herschel, Draper); by an exposure to white light followed by bathing in a solution of an oxidizing agent and exposure to the spectrum (Abney); by the use of stained plates (Waterhouse); by a partial development and subsequent treatment with a silver nitrate (Sabatier); by the action of white light during development (Sabatier, Nipher); by very slow development of an under-exposed plate (Guébhard); by the addition of thiocarbamide, etc., to the developer (Waterhouse); by very short and very intense exposures with a subsequent short exposure to diffused light (Clayden, Wood); by cathode rays followed by sunlight (Goldstein); by positive light of two intensities (Goldstein).

4. The stronger the developer and the longer one develops, the more easy it is to obtain a reversed image. Very slow development of an over-exposed plate will give a normal image. The latent, reversed image is destroyed more rapidly than the latent, normal image by bromine, nitric acid, ammonium persulphate, chromic acid, etc.

5. With pure silver bromide collodion and chemical development, solarization begins at approximately the same time as the visible blackening of the silver bromide; but with silver bromide collodion containing silver nitrate, visi-

ble blackening takes place long before any solarization image is formed.

6. The visible blackening of the plate which causes the second reversal is probably due to allotropic or metallic silver.

7. Silver nitrate and potassium nitrate apparently prevent solarization when added to the film before exposure. It is probable, however, that the rapid reduction to silver in presence of these 'halogen absorbers' masks the solarization.

8. When a plate is exposed to light during development, it makes no difference whether the light falls on the plate from above or below. There is therefore no screening effect due to the partially developed image (Nipher, Trivelli).

9. In most cases there is a simple quantitative relation between the original exposure and the amount of light necessary during development if the plate is to be brought into the 'zero state' (Nipher). As no experiments have been made with approximately monochromatic light, it is not known how far the form of the relation depends on any change in the color-sensitiveness of the plate.

10. The latent reversed image can be developed physically. If a plate is fixed first and then developed physically, we may get a normal image or a reversed one, depending on the conditions of the experiment.

11. In the developed plate, the reversed image is chiefly in the lower layers.

12. According to Eder there are three images on an undeveloped over-exposed plate; a latent normal image, a latent reversed image, and a normal silver image. According to Homolka there are two latent normal images.

13. When a platinum electrode, coated with silver bromide, is dipped in a bromide solution and exposed to a moderate light, it becomes the cathode. When a stronger light is used, the platinum electrode will sometimes tend to become the anode (Luggin).

14. A film of silver iodide swells and clouds when ex-

posed to light. No measurable change in chemical composition takes place and the rate of clouding under the influence of light seems to be increased by the catalytic action of oxygen, iodine, etc. (Scholl).

15. The substance forming the latent, reversed image is a silver oxybromide of the general type $AgBr_xO_y$ (Abney, Eder).

16. There is no such thing as a latent reversed image. The phenomena are due to the regeneration of silver bromide.

17. The latent reversed image is a reduction product of silver bromide (Lüppo-Cramer).

18. The developable image consists of silver bromide and an α-silver sub-bromide which is itself reduced by the developer but which acts as a catalytic agent, causing the developer to reduce the silver bromide. This α-silver sub-bromide can be reduced by light to a β-silver sub-bromide which is also reduced by the developer but which has no catalytic properties. Solarization occurs when the α-silver sub-bromide has been changed in the high lights very largely to β-silver subbromide and this change has not taken place to any great extent in the shadows (Trivelli).

19. The phenomenon observed by Herschel, Abney, Clayden, Wood, and Nipher are not to be considered as solarization (Trivelli).

20. The Waterhouse process with thiocarbamide in the developer gives pseudo-positives (Nipher).

Cornell University

CUPROUS HYDROXIDE AND CUPROUS OXIDE

BY H. W. GILLETT

Previous work by Mr. Miller and others has shown that when a solution of NaCl is electrolyzed between copper electrodes, yellow cuprous hydroxide is formed if the electrolysis is carried on at low temperatures, say below 60°, that at boiling temperature scarlet cuprous oxide is formed, and that at intermediate temperatures, products of intermediate colors are formed. A high current density produces a more deeply colored product, other things being equal. The concentration of the NaCl is without much effect. Colloids give a lighter colored product when the electrolysis is carried on in their presence.

Work by Mr. Miller showed that the size of the particles runs parallel with the gradations of color, but analyses of these products of different colors show that they are more probably of different colors because of their different content of yellow hydroxide and scarlet oxide, than that this color variation is due solely or chiefly to the size of the particles.

Microscopic examination fails to show any trace of inhomogeneity, so it seems probable that there is a series of solid solutions of the oxide and hydroxide. Owing to the fact that the equilibrium is practically irreversible, the definite proof cannot now be given.

Some attempts were made to precipitate the red oxide cold, electrolytically or chemically.

A solution of cuprous chloride in NaCl was precipitated by pouring into a solution of NaOH. It was found that with *very* concentrated caustic, the oxide was obtained cold, but that heating had much more effect on the formation of the oxide than the concentration. The direction of pouring, *i. e.*, the relative concentrations of the chloride and caustic seemed to be without effect. Heating the hydroxide after precipitation was without noticeable effect.

The yellow hydroxide, made electrolytically in the cold,

was boiled for some 80 hours, but no dehydration was shown, either by change of color, or on analysis. Samples of the hydroxide treated with NaOH of varying concentration showed little dehydration, save in the very concentrated NaOH solutions. With saturated caustic, or with solutions of such strength as to attack filter paper very energetically, there was some dehydration. The more dilute solutions showed but very faint signs of action. Heating to 95° for half an hour did not aid matters at all. In all the cases where the CuOH was treated with fairly strong NaOH, considerable hydroxide went into solution as shown by the blue color. This solution was not investigated.

In all cases now to be described, copper electrodes, 10 percent NaCl electrolyte, 7–8 amp/qdm, and 20° were the conditions unless otherwise stated.

Since the chemical precipitation had shown that the product was redder the more concentrated the caustic, the effect of adding NaOH to the electrolyte was first tried. When the strength of the caustic soda was 0.5 percent or stronger, oxygen was given off at the anode and no precipitate was obtained. The copper anode apparently becomes passive under these conditions.

With 0.05 percent NaOH in the electrolyte, the bulk of the precipitate was the light yellow of the hydroxide, but one tiny spot of scarlet oxide formed on the anode, on the side farther from the cathode. Similar results were obtained with 0.025 percent NaOH. In neither case was the oxide 1/1000 of the total precipitate.

N/100; N/250, N/500, N/1000 HCl electrolytes, with the usual 10 percent of salt were tried, with results not varying from those obtained in neutral solutions.

In neutral solutions more or less spongy copper was precipitated at the cathode, and the electrolyte became more or less alkaline. With high current density at the anode, the product was a trifle darker than under normal conditions. No difference was observed when a high cathode current density was employed.

Very rapid stirring of the electrolyte was tried, and gave a distinctly darker product than without agitation, but not enough to indicate 5 percent of the oxide in the precipitate.

Stirring with the addition of scarlet oxide to furnish crystallization nuclei was tried, but gave no better results.

The alternating current gave no precipitate at all.

With conditions as usual, save that the temperature was 50°, still too low to give the oxide normally, and a porous porcelain pot as diaphragm, no precipitate was obtained at first, but finally the usual yellow began to form at both inner and outer surfaces of the pot. The anode liquor was poured into the cathode liquor, the resulting precipitate being slightly lighter in color than that normally obtained electrolytically. With an extraction thimble of paper as diaphragm, yellow hydroxide was formed both within and without the thimble, that in the thimble (anode compartment) being a trifle darker than that without (cathode compartment). In the filter paper of the thimble itself, however, unmistakable scarlet oxide was formed. This experiment with the thimble diaphragm was repeated at 20° and similar results obtained. The position of the oxide in the thimble was not conclusive as to whether it was formed at any particular layer of the solution, or any particular distance from the anode, though it seemed that perhaps more was formed at the bottom and rather near the anode.

Some experiments were next made without a diaphragm to test the effect of varying the position of the electrodes. With the electrodes vertical and very close together, not over 5 mm apart, the precipitate was slightly darker than normal, much resembling that with rapid agitation, but not dark enough to indicate any considerable percentage of oxide.

With L-shaped electrodes and the anode above, the precipitate was of the usual light color. No oxide was observed on either electrode. The liquid became very alkaline and some copper was precipitated at the cathode. Some was also precipitated in the previous case, where the liquid was only slightly alkaline at the end of the run.

With L-shaped electrodes and the cathode above, some copper was precipitated, and the liquid became very alkaline. The precipitate was of the usual light color, but on the outer portion of the anode were small areas of scarlet oxide. Neither in this case, or in any other, was the total yield of oxide 1/100 that of the total mass of hydroxide.

To test the idea that dehydration might be brought about by endosmose, yellow hydroxide, made electrolytically, was packed in between two rather closely fitting porous cups, between both sides and bottoms. L-shaped electrodes were used, and a little NaOH added to the salt electrolyte in the inner, anode, compartment. No change in color was observed in an hour's run.

When the oxide appears on the anode, it is in small irregular spots, as if there were some local condition of the electrode producing it. Since, in the chemical and electrical precipitation, heating is of most effect in inducing the formation of scarlet oxide, we might think that a local adhesion of undissolved cuprous chloride, which usually could be seen on the anode to a slight extent if the solution was not agitated, might have increased the resistance at that point to such an extent that the Joulean heat might have raised the liquid just at that portion to a high enough temperature for the oxide to be naturally formed. But this local heating could hardly exist in the fibres of the thimble diaphragm.

Hence while these experiments show that a small amount of cuprous oxide *can* be formed electrolytically, cold, they also show that it is at least not easy to find conditions under which the yield will be quantitative. Since the oxide is very easily formed at temperatures around 100°, if it were desired to precipitate the oxide electrolytically with a NaCl electrolyte and copper electrodes, heating by a steam coil, or by blowing live steam into the solution would seem to be the easiest way.

This work was suggested by Professor Bancroft and was carried on under his supervision.

Cornell University

CONSTANT CURRENT ELECTRO-ANALYSIS

BY H. W. GILLETT

LeBlanc[1] considers that the separation of metallic ions from an electrolyte goes on in a stepwise manner, the ion that is most readily deposited, *i. e.*, has the lowest decomposition voltage, and that ion only, being deposited until the number of ions of that metal is no longer sufficient to carry the current for the current density used, when the next in order of decomposition voltages begins to deposit, and so on. In the electrolytic separation of copper from zinc in nitric acid or sulphuric acid solution, for example, the copper is deposited till the solution becomes so impoverished in copper ions that they can no longer carry all the current, when gassing begins and hydrogen is liberated. Since the acid is not used up, the solution does not become impoverished in respect to hydrogen ions, and so, although we may be using a voltage across the terminals which is far above the decomposition voltage of zinc, the zinc is never deposited because the hydrogen is more readily freed and consequently the voltage at the cathode does not reach the value for zinc provided the solution is stirred effectively. Even if a trace of zinc were to precipitate, it would at once form a couple with the copper and would go into solution again. To this position of the decomposition voltage for hydrogen is due the possibility of all constant current methods of electrolytic separation now in use.

But if we wish to separate two metals whose decomposition voltages both lie below that for hydrogen, we fall back on a constant voltage method of separation, or else use another electrolyte in which the decomposition value for hydrogen does lie between those of the two metals in question. According to the theory, however, if there is present a sufficient number of ions of a metal, say B, whose decom-

[1] Le Blanc: A Textbook of Electrochemistry, p. 297, 1907 Ed.

position voltage lies between those of the two metals we wish to separate, say A and C, we should be able to stop the electrolysis when all A is deposited, before C has begun to deposit, and when B is partly deposited and partly in solution. Without this middle or protecting metal no separation would be possible, for even if we were able to throw the switch at the psychological moment when the last ion of A had just been deposited, some C must have deposited also, for that last ion of A would be able to carry only the number of electrical charges it is entitled to from its valency, and other ions, *i. e.*, those of C, must come into play in order to keep a measurable current passing. If the voltage between the electrode was below the decomposition voltage of C, then with the discharge of the last ion of A, the current must automatically cease, and the case would be that of a constant voltage separation. So to make it a constant current separation enough of B must be present to carry the current for some time after A has been quantitatively deposited, and before by its own impoverishment it calls upon the ions of C to aid in carrying the current.

One other condition must be fulfilled in order to keep C wholly in solution. If, after all A is deposited, at some portion of the cathode, B becomes locally and momentarily impoverished through insufficient stirring, so that an ion of C is deposited, C owing to its position in the voltaic series above that of B should redissolve and precipitate in its place an ion of B. In order to do this, the metal C must not be passive in the electrolyte used, *i. e.*, it must be able to precipitate B from its solution in that electrolyte.

If then, with the question of passivity out of the way, we have a large enough excess of a metal with a decomposition voltage intermediate to those of the two metals we are separating, so that we may have time to stop the electrolysis after we find by chemical tests that the metal first deposited is all out of the solution and before the last metal to separate begins to come out, we should be able to use a constant current method with a voltage across the terminals

higher than the decomposition voltage of any metal in the solution.

For several years Prof. Bancroft has explained the theory as outlined above in lectures to his students, but no actual example of any protective metal other than hydrogen has been at hand. Two years ago the writer attempted, under his direction, to find an instance, taking as a basis the values given by Root[1] for the decomposition voltages in ammoniacal tartrate solutions of Ag 1.0, Pb 1.3, Cu 1.65 at 60°. Here lead should serve as the protecting metal. The actual decomposition values obtained were lower than those given by Root, a plentiful deposit of copper being obtained at 1.35 volts. But when this voltage was exceeded for any length of time, even in the presence of a large excess of lead, copper was deposited, which seemed contrary to the theory. The separation was satisfactory as a constant voltage method.[2] This apparent contradiction of the theory was cleared up by finding that in the ammoniacal tartrate the copper became passive, and that a copper strip would not precipitate silver or lead from this solution.

Root gives the following series in phosphate solution at 60°. Ag 1.3, Cu 1.6, Pb 2.2, H 2.25. Here copper might serve as the protecting metal between silver and lead. To test this case the power of lead to precipitate silver and copper from phosphate solutions was tried, and it was found that these metals were precipitated. In attempts to make up the lead solution used by Root it was found that the amount of H_3PO_4 specified was insufficient to keep all of the lead in solution at 60°, hence about twice the amount he employed was used.

The following solution was made up. 0.13 gram of $Pb(NO_3)_2$ was dissolved in 1 cc water, 6 cc of 85 percent H_3PO_4 added, and the whole heated to 100°, a clear solution being obtained. This was diluted to 125 cc with hot water and kept at 60°, no precipitate appearing under these circum-

[1] Root: Jour. Phys. Chem., 7, 462 (1903).

[2] Cf. Jour. Phys. Chem., 12, 26 (1908).

stances. On electrolysis of this solution at 60° in a Classen dish with a rapidly rotating anode at 0.5 amp. and 2.4 volts between the electrodes, a copious deposit of lead was obtained, showing that we were above the decomposition voltage for lead.

A solution was then made up of 0.13 gram $Pb(NO_3)_2$ dissolved in 1 cc water, 6 cc 85 percent H_3PO_4 added, heated as before, and diluted to 125 cc with a hot solution of 118 cc water and 0.12 gram $AgNO_3$ and 1.40 gram $Cu(NO_3)_2$ 6 aq. This was electrolyzed at 0.75 amp. 2.6–2.8 volts and 60° with a rotating anode. At first there was obtained a good adherent deposit of silver, then some adherent red copper, and then a non-adherent coating of rather dark "burnt" copper. When the solution gave no further test for silver with HNO_3 and HCl, the run was stopped, the deposit washed, the non-adherent deposit filtered and washed, and both parts of the deposit dissolved in HNO_3. H_2SO_4 gave no test for lead from the cathode deposit. The electrolyte gave no test for silver, and still contained much copper. There was a trace of PbO_2 on the anode.

Another run was made on a solution of the same composition save that it contained 2.0 grams of copper nitrate. This was electrolyzed at 1 amp., 2.5–2.9 volts at 60°, rotating anode, till all silver was deposited. On testing the electrolyte and cathode deposit on completion of the run, the electrolyte as before contained no silver and much copper, while the cathode deposit was free from lead both by the H_2SO_4 test, and by microchemical test with KI, extraction on the slide with hot water, and examination of the decanted and concentrated solution for PbI_2. No lead was found. A mere trace of lead nitrate added to the solution of the cathode deposit gave a good test for lead.

No attempt was made to obtain an adherent deposit, or to determine the amount of copper needed to hold up the lead, since no one would care to add copper to a solution in which he wished to separate silver and lead when so many easier methods are available. This method is of no value in

itself, but is of interest solely in showing that the theory does hold. In the usual electrolytes the number of separations possible by use of a protecting metal is very small because of the complications that may be introduced by the formation of an alloy, amalgam or solid solution;[1] but, in the more uncommon electrolytes, voltaic series may be found such that it may be possible to work out some practical as well as theoretical constant current separations by the use of some other protecting metal than hydrogen.

This work was suggested by Prof. Bancroft and carried out under his direction.

Cornell University

[1] Bancroft: Trans. Am. Electrochem. Soc., **3**, 89 (1903).

NEW BOOKS

Recent Advances in Organic Chemistry. *By A. W. Stewart. With an Introduction by J. Norman Collie. 15 × 23 cm, pp. xi + 296. New York: Longmans, Green & Co., 1909. Price: $2.59 net.*—The introduction by J. Norman Collie is so good that it is worth quoting in full.

"At the present time it is not altogether easy to say on what lines a text-book of Organic Chemistry should be written. To state in the preface that the author "hopes it will supply a long-felt want" is not always an injudicious method of announcing the author's belief in the readers of text-books. For if the "long-felt want" of the public is to have a restatement of all the old facts once more, with nothing new, no critical faculty shown, and an obvious lack of evidence that the book can be used to broaden our outlook on other sciences as well as chemistry, then no doubt the desire of the public for the time being is satisfied.

"It certainly is to be regretted, however, that so many books on Organic Chemistry are published regardless of the fact that Organic Chemistry is a growing science. If one wants to know a new piece of country, to obtain a large number of photographs all taken from the same place is obviously a foolish thing to do. Yet book after book on Organic Chemistry is published, covering the same ground, with a fine disregard of the fact that to the pioneers the outlook is constantly changing. A book that has practically nothing new in it except the description of a few more compounds is unnecessary. Fortunately, however, there are some text-books which are not mere narrations of facts, and which do point out not only what has been done, but what might be accomplished, and which do make the reader think.

"At no time, however, is a change wanted in the method of writing text-books more than at present. Deluged as we are with unnumbered facts that have often neither explanation nor obvious connection with one another, Organic Chemistry has become a vast rubbish heap of puzzling and bewildering compounds. The sanguine chemist expresses a hope that some day, perhaps, a few of these may be useful. All knowledge ought to be useful, even that obtained by the manufacture of the thousands of new substances which are annually produced in chemical laboratories. But where is it to stop? When one looks at Beilstein's "Handbook" or Richter's "Lexicon," or takes up a current volume of any chemical journal, how many of the compounds or the papers are of interest even to the most enthusiastic chemist? The game of permutations and combinations goes on, the chief object apparently being merely to supplement the already existing myriads of laboratory-made organic compounds.

"How, out of all this undigested mass, is the writer of a text-book to glean what is of interest or tell what ought to be taken and what left? The result is that many text-books are not much more than abridged chemical dictionaries. The only tax on the reader's mind is to remember as many facts as possible. The text-book is rare that stimulates its reader to ask, Why is this so? or, How does this connect with what has been read elsewhere?

"Indeed, it is not inconceivable that a useful textbook might be written on the constitutional formula of a single organic compound; for instance, alcohol. Its manufacture and physical properties would have to be considered. This would necessitate a knowledge of many typical organic compounds, and also of many kinds of reactions. The evidence thus obtained could then be summed up for the purpose of expressing all these facts by the chemical formula. Here the theory of the constitution of organic compounds would have to be dealt with, beginning with the idea in vogue at the beginning of the last century: Berzelius' Electro-chemical Hypothesis, of how the nature of the elements present had the chief influence on the properties of the compound; Dumas' Type-theory, and how he was the first (about 1840) definitely to recognize the arrangement of the atoms in the molecule; how this idea took about a quarter of a century to get into the text-books; how Frankland, in 1852, started the idea of valency, from which sprang the modern ideas of chemical structure and linking of atoms; how Kekulé first definitely put forward the idea of the quadrivalence of carbon; how Crum Brown, in 1865, suggested the present form of graphic formulae and pointed out that they were "not to indicate the physical but merely the chemical position of the atoms." All these ideas have more or less centered round alcohol and its derivatives; and any one who carefully had followed the reasoning that led to these various mechanical methods for representing by a chemical formula the molecular structure of organic compounds would be in a position easily to recognize that our present ideas must in future suffer change just as they have done in the past.

"Berzelius' ideas were those of a great mind; but in his day narrower theories were necessary for the more detailed development of chemistry. Dumas' Type-theory, on the other hand, was too narrow; it was a very restricted system of classification, and one that led to many false analogies. Up to the present day, the Frankland-Kekulé conceptions of valency and graphic formulae have held their own, but there are signs that these, too, will have to be modified; physical as well as chemical properties will have to be accounted for. The present volume should be of great use to students of organic chemistry. The subject-matter is put in an eminently lucid form that enables the reader easily to follow all the arguments, while at the same time his critical faculty is stimulated. The book, moreover, is unlike so many modern text-books in that it is not a mere compilation of facts; several novel theories on organic chemistry are dealt with, theories that up to the present can hardly be said to have assumed definite shape, but which rather point to the paths along which the pioneers of the science are likely to go in the immediate future."

The chapters are entitled: Main currents in organc chemistry during the last half century; the Grignard reaction; asymmetric synthesis and new methods of producing optically active compounds; the polyketides and their derivatives; the polymethylenes; the monocyclic terpenes; the dicyclic terpenes; the olefinic terpenes; the synthetic alkaloids, some alkaloid constitutions; the polypeptides; the chemical action of light; some theories of addition reactions; unsaturation; conclusion.

In the first chapter the opening paragraphs and the last two are excellent.

"Speaking exclusively of observational and experimental sciences, it is

obvious that progress can be accomplished only at the cost of destroying or modifying current theories; for if a theory suffices to explain facts discovered after its promulgation, knowledge may be increased; but there is no true progress unless our general outlook is altered. Thus in science we have an alternation of two courses: in the first the aim is the accumulation of facts and yet more facts; while the second is directed towards classifying these facts in the most convenient manner. At irregular intervals some facts are discovered which cannot be fitted into the accepted scheme of arrangement and in order to make room for them the scheme has to be altered and recast into some new form.

"Thus in every science which is at all progressive there must arise from time to time conflicts between the older generation of workers and the leaders of the new; for, to those who have grown up along with it, a theory generally becomes invested with a sort of sanctity which is quite out of keeping with its true make-shift character. The longer a theory stands the harder does it become to shake it, and the greater is the tendency of the science to become stereotyped. There is another side to the question. Without any disrespect, it may be said that the majority of scientific investigators are not possessed of strikingly original minds—we cannot all be Pasteurs—and hence there is a very pronounced tendency to take things as they are and work along the beaten track rather than to push out in the wilderness and risk the chance of losing the road altogether. Thus round every theory there grows up a little band of workers, whose one aim seems to be to accumulate evidence confirming their favorite hypothesis; and in this way the theory gains a considerable weight of supporting data. On the other hand, the solitary worker who happens to differ from the majority of his fellows has to overcome a tremendous weight of unconscious prejudice before he is able to obtain even the semblance of an impartial hearing. In spite of these difficulties, however, progress is made."

"When we look at the present condition of organic chemistry it is rather discouraging. Everything seems to be cut and dried as far as the theory of the subject is concerned, and on the practical side the main tendency seems to be merely to confirm current theories. It is self-evident that we can make no progress by confining ourselves to the confirmation of the views which pass muster at present. If any advance is to be made, it must be begun by investigating those phenomena which do not agree with the standard theory; and as an instance, we might point to the case of the ionic hypothesis and the ordinary organic reaction. There is, however, another direction in which we may look for a line of research. It is customary in text-books to assume that "water adds on in such and such a way," or, "the bromine atom attaches itself in the usual way to the tertiary carbon atom;" many such expressions can be found, but it never seems to occur to the ordinary person that to state a fact is not to offer an explanation, and while we are all sufficiently glib in describing how a reaction takes place, very few of us seem to give a thought to the problem of why the reaction takes that particular course rather than another. We have thus accumulated an immense mass of data concerning the results of reactions, but very little indeed with regard to their causes. It seems obvious that if organic chemistry is to get a new lease of life, some attention must be paid to such questions as these. Of course the investigator who takes up such

problems will have to invent a new set of methods; but the aim in view would be worth a little trouble.

"At the present day it appears to be the fashion to suppose that certain views are so firmly established that no research into their foundations is worth the labor expended on it, and consequently investigators devote much time and energy to the examination of highly complex substances while simpler compounds are supposed to be "worked out." In the same way it was supposed for many years that the composition of the atmosphere was well known, until the work of Ramsay and Rayleigh showed how little we knew of even this common mixture. With this object lesson before them, it is to be hoped that more organic chemists will find time to investigate some of the problems which are passed over by the mass of workers who seem to rank a label in the same category as an explanation."

In the chapters on asymmetric syntheses, the author sums up as follows:

"The task of producing a laboratory parallel to plant syntheses has been accomplished; we may not have actually produced the same substances as the plant forms within its organism, but we have certainly utilized analogous methods, and obtained similar results. In the succeeding chapters it will be shown that we can carry our parallel further than the mere question of optical activity, and that, beginning with very simple groups, we can build up many vegetable and animal products by reactions, which probably approximate closely to those which take place within living organisms."

In the chapter on polyketides we find the following instructive paragraphs:

"Broadly speaking, plants differ from animals in that they can nourish themselves with water and carbon dioxide alone, while the animal kingdom requires the intermediation of vegetables and other organized matter. The substances which lie at the base of all syntheses of organized tissues must therefore be simple compounds of carbon, hydrogen and oxygen. Once having synthesized such substances, the plant as will be shown later in this chapter, could easily build up derivatives of the aliphatic, aromatic, and heterocyclic series.

"At the beginning of the previous chapter it was pointed out that, given formaldehyde, sugars may be produced by the action of alkalis, and many such samples of the production of complicated natural bodies from very simple substances are known. In the present chapter we shall confine ourselves to derivatives of one class; but as this class is interwoven with all the main groups of organic compounds, it will serve as a skeleton from which the relations between apparently quite dissimilar groups can be deduced. At the same time, it must be borne in mind that our laboratory synthetic methods differ in the main from those employed in the living plant. While we, in our syntheses, start from the same elements as the plant does, we usually build up our substances step by step, proceeding from simple to complex. The plant appears to act differently; for it, apparently by condensation, polymerization, or some such process, converts its simple starting substance into an extremely complicated derivative, which then decomposes, yielding those products which have been identified in saps and tissues. Again, while most of our ordinary laboratory reactions can be applied to the production of substances which are found in plants, it is obvious that the plant must obtain the same result in a much simpler manner. For instance, when we wish to attach side-chains to

a benzene nucleus, we employ aluminium chloride in the Friedel-Crafts reaction; but such a reagent could not exist in a plant. Further, a great number of our laboratory reactions require the use of high temperatures, which would be fatal to plant life.

"When we examine all the compounds known to us in the domain of organic chemistry, it is inconvenient for our present purpose to regard them from the point of view of text-book classification. What is of chief importance to us is the question, Can they be made to react easily? From this point of view we divide compounds at once into two groups, the saturated and the unsaturated, the latter being the reactive ones. This is, of course, speaking in very general terms, for many saturated substances are quite reactive. Now, among unsaturated substances we can again distinguish two classes—the desmotropic and the non-desmotropic. Of these, the desmotropic class is by far the most reactive. The cause of this is obvious, for if a non-desmotropic substance be brought into the presence of a reagent, it has only one way in which it can react, and if combination does not take place the matter ends; with a desmotropic compound, however, if the first form fails to attack the reagent, there is always the possibility that the second form may be more successful.

"In nature, we find many desmotropic and tautomeric substances; but the preponderating class is that which contains compounds of the type

$$R—CO—CH_2—R' \longrightarrow R—C(OH) : CH—R'.$$

"This 'keto-enol' type is very widely distributed among naturally occurring substances; it is found in nearly every important class of compounds, from the purine group to the terpenes; and, further, its one form is converted into the other isomeride more easily than is the case with practically any other mode of isomeric change."

The chapters on the terpenes and the alkaloids are rather difficult reading for anybody except the specialist; but in the chapter on the chemical action of light the following passage is worth quoting:

"Usher and Priestley have shown that if the chlorophyll be removed from plant-leaves, it may be used in conjunction with enzymes to produce photosyntheses which closely resemble those carried on in the plant. For example, they were able to decompose moist carbon dioxide and synthesize formaldehyde and formic acid. The action of the chlorophyll, according to Macchiati, is similar to that of a sensitizer; leaves from which the ferment has been removed are unable to break down carbon dioxide, nor can the ferment itself act unless chlorophyll is also present."

There is a great deal that is instructive in the chapter on unsaturation as the following extract indicates.

"When we examine the matter closely, we find that the foundations of theoretical organic chemistry are a series of labels by means of which we endeavor to conceal our ignorance of the fundamental phenomena of the subject. Of these labels, none is used more indefinitely and at random than the word 'Unsaturation.' It seems not without some interest, therefore, to examine the various phenomena which are usually ascribed to the presence of this property, and to see how far we can attain to some clear idea of what we mean by the word.

"In the first place, let us ask ourselves what we mean by an unsaturated compound. The picture which is formed in our mind by these words usually represents two molecules uniting together, and one of these we are accustomed to call an unsaturated substance. But before going further we are faced by a difficulty, for there seems no reason why we should consider one of the two molecules unsaturated and the other saturated. For example, if a molecule of bromine unites with a molecule of ethylene, we call ethylene an unsaturated hydrocarbon, but we do not regard the bromine molecule as unsaturated in the same sense. If we examine the matter more closely, however, the difference between the two cases becomes clear. When ethylene takes up an atom of bromine the ethylene molecule is not completely disrupted; part of it remains as it was, for the two carbon atoms are still united, and each bears the same number of hydrogen atoms as before. With the bromine molecule, however, no trace of the original structure remains. Evidently our idea of an unsaturated compound must be extended; it is no longer sufficient to say that it is "a molecule capable of uniting with another molecule;" but we must add, "without a disruption of its original structure." This definition covers practically every case which has any claim to be considered; and we may therefore adopt it and proceed to inquire if we can distinguish further between the various classes of substances which come from within the definition.

"The simplest type of an unsaturated compound with which we can deal is a component of a double salt. Here the amount of unsaturation is very slight, for we may decompose the saturated body (double salt) into its components again by a mere lowering of the temperature. We need not go into any details with regard to these substances, as except in such cases as the tartrates and the double compounds of triphenylmethane they do not fall within the range of organic chemisty.

"The second class of unsaturated compounds includes those in which the addition of new atoms takes place at one atom only, as, for example, trimethylamine, dimethyl-sulphide, dimethyl-pyrone, etc. In this case the least possible change in the general structure of the molecule takes place during the addition reaction.

"The third class of unsaturated compounds contains those bodies which are capable of uniting with two atoms, but in which addition takes place at two adjacent atoms. The ethylene series, the ketones, and the nitriles are instances of this type.

"There is another class of bodies which, while resembling the last-mentioned one, in so far as their capacity of adding on only one pair of atoms is concerned, differs from it in the manner of addition, for instead of the two new atoms attaching themselves to two adjacent atoms, as in the ethylene class, in this new series they attach themselves to non-adjacent carbon atoms. The polymethylenes are a case in point.

"Finally, we come to the acetylene class, in which we are able to unite four new atoms to two of the carbon atoms of the unsaturated compound.

"Thus we have divided unsaturated bodies into the following five classes:

1. Components of molecular compounds.

2. Compounds of mono-valent iodine, divalent sulphur, selenium, tellurium, oxygen, etc., trivalent nitrogen, phosphorus, antimony, etc.

3. Compounds containing groups like C: C, C: N, C: O.
4. Cyclic compounds.
5. The acetylenes.

"Of course, it is quite easy to multiply the possibilities by combining in one molecule representatives of each class, as in the case of mesityl oxide, for instance; but if we reduce the question to its simplest form, the above series will serve as a mode of classification.

"Before entering into a consideration of these classes, however, we must deal with two other points which arise. What we call an unsaturated substance may be unsaturated with regard to one agent, and quite saturated towards another. For instance, if we take the substances in Class 3, though all of them are unsaturated with respect to nascent hydrogen, they differ in their behavior towards bromine, ammonia, or water. Again, it is sometimes found that a compound may behave as a saturated or an unsaturated substance according to the conditions under which reactions are carried out. For example, in sunlight benzene forms addition products much more easily than in the dark. Thus there are fine differences for which we have no corresponding technical terms."

In the final chapter there are some interesting paragraphs, though many will not agree with the point of view.

"It often happens that one meets with a series of apparently related facts, and one is anxious to put forward some plausible explanation which will make the connection between them clear. Under these conditions we may proceed on either of two alternative lines. For instance, on the one hand we may put forward some general idea which, without troubling about details, will allow us to regard the matter from a broad point of view; or, on the other, we may set up some mechanical model which will, as far as possible, reproduce the phenomena we set out to explain.

"At the first glance, the former method seems the more likely to lead near the truth; but consideration will show us that this is not the case. Suppose that our general idea covers all the facts known at a given time, and is quite comprehensible when considered in relation to these facts. Then let us imagine that some new facts are discovered which do not quite agree with the general idea. As a result, the general idea is widened to include these facts, and thus it becomes more vague than it was before. After this process has continued for a time, the general idea has widened insensibly, until it ceases to have any definite meaning. It eventually becomes a mere rag-bag of views or an amorphous mass which can be squeezed to fit any need. Naturally, also, it has ceased to have any value from the scientific point of view—it can no longer stimulate us in research, nor can it aid us in our classification of facts.

"With a mechanical hypothesis, on the other hand, we have something definite, which either does or does not fit the facts. If it fits them, well and good; but as soon as it ceases to agree with our data we discover the inadequacy, and can discard the mechanical model, replacing it by another which is more in accord with our increased knowledge. We cannot, as in the case of the general idea, expand it and make it more vague, but we can expand it while retaining its definiteness.

"The difference between the two methods can be seen by comparing the system of 'energetics' put forward by Ostwald and others with the modern

structural (mechanical) theories of organic chemistry. It is quite certain that no application of the purely 'energetic' views to organic chemistry could ever have carried the science to the point at which it now stands; while, on the stereochemical side, 'energetics' seem to hamper rather than aid some minds in the attempt to grasp the phenomena with which we have to deal."

One fallacy in this argument is the assumption that the only alternatives are a general idea with no details and a mechanical model. There are other fallacies, but it is not worth while to emphasize them. This is a good book both as regards plan and workmanship. *Wilder D. Bancroft*

The Nature of Enzyme Action. *By W. M. Bayliss. Monographs on Biochemistry. Edited by R. H. Aders Plimmer and F. G. Hopkins. 15 × 25 cm; pp. viii + 90. New York: Longmans, Green & Co., 1908. Price: $1.00 net.* —The headings of the ten chapters are: catalysis in general; enzymes as catalysts; chemical and physical properties of enzymes; general methods of preparation and of investigation; reversibility of enzyme action; the velocity of reaction and the various conditions affecting it; the nature of the combination between enzyme and substrate; co-enzymes and anti-enzymes; zymogens; oxidation processes and certain complex systems.

On p. 75 the author sums up the book as follows:

"The living organism is enabled by the use of enzymes to bring about, under ordinary conditions of temperature and moderate concentrations of acid or alkali, many chemical reactions which would otherwise require a high temperature or powerful reagents.

"A careful study of these enzymes shows that they obey the usual laws of catalytic phenomena. Certain deviations from the behavior of most inorganic catalysts are found to depend upon the colloidal nature of enzymes, so that the reactions take place in a heterogeneous medium and the various phenomena depending upon surface action come markedly into play.

"As they are sensitive to heat and more or less rapidly destroyed by it, they show the phenomenon of a so-called *optimum* temperature. This destruction by heat is, in all probability, due to their organic colloidal nature.

"So far as we know, the reactions catalyzed by enzymes are reversible in nature, but since, as investigated *in vitro*, they take place in presence of excess of water, the equilibrium position is usually very near the stage of complete hydrolysis. Owing to this reversible character of the reactions, it follows that enzymes have synthetic action.

"Reasons are given for the belief that the 'compound' of enzyme and substrate, generally regarded as the preliminary to action, is of the nature of a colloidal adsorption-compound.

"The existence of a relation of this kind explains the exponential form of the law correlating the concentration of enzyme with its activity.

"Autocatalysis, positive and negative, plays a considerable part in the changes of activity of an enzyme during the course of its action. These changes of 'activity' are the main factors in the deviations of the form of the equation for the velocity of reaction from the simple unimolecular formula, when the reaction, as is usually the case, takes place in presence of excess of water."

Wilder D. Bancroft

A MODIFIED OXY-HYDROGEN GAS COULOMETER

BY J. W. TURRENTINE

In taking measurements of quantity of electricity two methods may be chosen—either the determination of current strength through the duration of a definite time interval, the product of amperes into time giving the number of coulombs, or the determination of the decomposition products liberated, in accordance with Faraday's second law, from solution by the current.

The first method requires the frequent reading of current strength as this is liable to fluctuations and frequent readings are necessary in order to obtain an average.

The second method is much to be preferred as only the final amount of the accumulated decomposition products is determined, so that the constant attention of the operator is not required.

The cell in which the electrolytically induced decomposition products are formed and the adjoined apparatus for accumulating them is styled a *coulometer* from the fact that it is employed in measuring coulombs, the name being an abbreviation of *coulomb-meter*. This term is not a new one, though, unfortunately, it has not yet come into general use in the electrochemical literature. It was first suggested by Prof. T. W. Richards as a substitute for the name voltameter, previously employed, to prevent the confusion between the names *voltameter* and *volt-meter*.

The measurement of coulombs, however, is not always the ultimate object of the use of the coulometer, but more frequently the determination of the current efficiency in some cell run in series with the coulometer is desired. The electrode products in the coulometer, which are measured, must then represent 100 percent efficiency. The electrode reactions must therefore be simple ones and must take place quantitatively.

The fact that in some coulometers the product to be

measured is metallic and in others is gaseous, gives us a simple method of classification. Of the former sort the silver and copper coulometers find the most general use, while of the latter, the oxy-hydrogen gas coulometers are universally employed. Expediency determines these forms, as they are the simplest.

When its use is possible the gas coulometer is preferable as the determination of the amount of the evolved gases may be made directly, either by weighing the cell before and after the electrolysis, as in runs of long duration, or by reading directly the volume of the evolved and accumulated gases. This obviates the inconvenience of drying and otherwise preparing the deposited metal to be weighed. Where very small measurements are to be made the gas coulometer is not only more convenient, but also more accurate, as the gas volumes can be read with a much greater accuracy than can a slight metal plate be weighed. While one coulomb accompanies the deposition of only 1.118 mg of silver and 0.3294 mg of copper, it liberates 0.12 cc of hydrogen. The gases liberated in the gas coulometers are either (*a*) allowed to escape through a depth of fused calcium chloride, or other desiccating agent, to dry them, the loss in weight of the cell representing the weight of the evolved gases, or (*b*) they are conducted from the cell into a eudiometer where they are measured, or (*c*) they are allowed to collect in the anode and cathode compartments of the coulometer respectively, and the volume of the oxygen and hydrogen are then read separately, or (*d*) they are allowed to pass together into a single, graduated tube where their aggregate volume may be read.

The first type of gas coulometer here mentioned (*a*), used in runs of long duration and when the loss in weight due to the evolved gases is quite appreciable, may be called the *weight* gas coulometer.

The second type (*b*) is quite undesirable because measurements made by means of it involve corrections for the downward pressure of the undisplaced liquid column in the eudiometer.

The same criticism also applies to many of the so-called two-armed coulometers (*c*), as this form is rarely supplied with a leveling bulb and the gas volumes consequently must be reduced to atmospheric pressure by correcting for the weight of the confining liquid columns.

The most convenient type (*d*) is represented by the Walter-Neumann, single tube coulometer. This is provided with a leveling bulb and therefore becomes a direct-reading instrument. This form is especially convenient for all current efficiency experiments when the electrode products are wholly, or in part, gaseous. The leveling bulb makes it possible to read the gas volumes, which are to be compared, at atmospheric pressure.

The Walter-Neumann coulometer is constructed of a single, upright tube, graduated, with an oblong, bulbous enlargement at its lower end, containing the electrodes, and is surmounted on its upper end by a stop-cock and capillary tube. The lower end is joined by means of a length of rubber tubing to a leveling bulb. The electrodes are corrugated plates of platinum foil mounted on thin platinum wires, the latter being sealed through the walls of the bulb and being terminated on the outside in small, tight coils, or loops. Electrical connection is made with the electrodes by hooking wires in these external loops.

The disadvantages of the apparatus are due to the fragility of the terminal wires and the glass seal which holds them. The platinum, terminal wires, being thin, are easily bent and in spite of care are soon broken off. This renders the apparatus useless.

Only poor contact is gotten with the terminal loops by hooking wires in them, yet this is the only means that may be employed for completing the electrical connection. If wires are fastened more securely in the coils, the latter are almost immediately broken off.

Poor connections with resulting imperfect contacts lead to local heating. The heat is conducted to the glass at the seal, which expands. Alternate expansion and con-

traction cause the glass to crack and the tube to leak. This also renders the apparatus useless.

When the tube is thus put out of commission the electrodes, perhaps the most expensive part of the apparatus, must be scrapped.

These objections, while few, are so serious that they render the apparatus entirely impracticable for frequent use.

The Walter-Neumann apparatus has been modified in such a way that these objectionable features have been obviated. While the same general shape of the older apparatus has been retained, the upright tube has been slightly narrowed to about five-eighths inch in diameter and lengthened, thus giving somewhat more accurate readings, and the graduations have been extended to 50 cc, from 40 cc in the old apparatus, thus increasing the capacity. The graduations, in 0.2 cc, are made from the stop-cock downward. Above the stop-cock extends a short capillary tube through which connection may be made with a gas burette, should an analysis of the coulometer gases be desired.

The lower, bulbous portion of the main tube has been greatly changed. This bulb is oblong and is three and one-half inches in length by one and one-half inches in diameter. Instead of the two platinum wires, it now carries, sealed in its walls, two side arms, or tubes, opposite each other and at an angle of 45° to the perpendicular, or longitudinal, axis of the tube. They are made to slope downward at this angle so that gas bubbles, carried into them by convection currents, can not become lodged. The side arms are five-eighths inch in diameter, they enter the bulb at a point one and three-quarter inches from its upper extremity and extend one inch outward, measured perpendicularly, from the lateral walls of the bulb.

The electrode plates are made of thin platinum foil and are deeply corrugated to enlarge their surface. They are one and one-fourth by one-half inch in dimensions and afford an electrode surface of at least a square inch on each face. Supporting them is a short section of platinum wire which is

sealed in a length of glass tubing of one-fifth inch external diameter and three inches long and which is welded to a piece of insulated copper wire about a foot in length and extending through the tube. The glass tubes are inserted through one-holed, rubber stoppers which fit the side arms.

The plane of the electrode plates makes an angle of 135° with the longitudinal axis of the glass tubes by which they are supported. These tubes when in place in the coulometer are, of course, parallel with the side arms through which they project. The side arms, being at an angle of 45° to the coulometer tube, and the electrode plates being at an angle of 135° to the side arms, the plates, when placed in position in the coulometer, are parallel to the coulometer tube and to each other. They thus face each other in a vertical position. By pushing the glass tubes through the stoppers, the electrodes may be brought closer together or farther apart, as desired.

This construction renders the electrodes easily detachable. This is especially desirable when they need cleaning.

In case the glass parts are broken the electrodes may be removed and placed in a new tube. This requires the purchasing of glass parts only after the initial acquirement of the electrodes. The length of copper wire is sufficient to furnish an elastic coil and to fasten to the external circuit by means of screw connectors. Thus perfect electrical contact is assured and local heating is avoided. Should breaks in the glass seals occur, they may be readily mended. As the electrodes are not subjected to very much wear, they should be quite long-lived.

The glass in the ends of the side tubes is thickened so that, if desired, the rubber stoppers may be wired in. This, however, experience has shown, is entirely unnecessary for ordinary solutions, as the friction of the rubber against the glass is quite sufficient to hold them firmly in place. When this friction is lessened by solutions of such substances as caustic soda it may be necessary at times to fasten the stoppers more securely.

The bulb of the coulometer below the side arms is drawn out, through a length of one and one-half inches, into a constricted portion whose walls are undulatory in outline. It terminates in an opening of a quarter of an inch in diameter. Over this opening fits the end of a section of rubber tubing which joins the coulometer tube with the leveling tube. The uneven walls of the constricted portion serve to hold the rubber tube in place.

For the leveling bulb employed in the old apparatus is substituted in the new, a leveling tube. Its advantages are that it is more easily handled and admits of a more accurate and rapid reading of the levels in the two parts of the apparatus. The leveling tube exceeds in capacity that of the graduated portion of the coulometer tube. It is about eleven inches in length and has an internal diameter of three-fourths inch.

The apparatus may be readily supported in ordinary burette clamps on iron stands, with which all laboratories are provided. Special stands, while they may be obtained and are convenient, are not at all necessary.

While the disadvantages of the Walter-Neumann coulometer have been overcome, at the same time, as has been abundantly evidenced by the specimens[1] in use the modified form does not suffer in comparison in point of compactness and neatness of appearance.

Cornell University

[1] Manufactured by Eimer and Amend, who have the drawings and specifications.

THE LOGIC OF THE FIRST LAW OF THERMODYNAMICS

BY J. E. TREVOR

INTRODUCTION

An exposition of thermodynamics, considered as a branch of theoretical physics, may be an account of the historical development of this subject; or it may be a logically ordered view of thermodynamic theory as it stands to-day. When the latter mode of exposition is adopted, the treatment naturally begins with an attempt to establish the general principles of the theory: the first law, the second law, the scale of absolute temperatures, the loss of work-availability in spontaneously occurring processes, and the analytical formulation of the thermodynamic laws. To present these matters in a clear and coherent way is a difficult undertaking; especially so when the first law is the topic in hand. The following pages outline an attempt to develop this topic in a strictly logical way.

It is assumed that the treatment will have been prefaced by an account of the fundamental notions of thermometry, this account including in particular the definition of temperature as a continuous function of some physical property of a selected thermometric substance.

PART I. THERMODYNAMIC CHANGES OF STATE

Physical changes of state

Physical science is concerned with 'physical phenomena,' with the mechanical, optical, thermal, electric, magnetic, chemical properties of bodies and the changes that these properties are observed to undergo. An ensemble of changes of the physical properties of an assemblage of bodies is a 'physical process.' For convenience of study, physical processes may be classified in accordance with the degree in which the physical character of the participating bodies is modified.

Thus, when a block of ice whose temperature is below the melting temperature of the substance is set in motion, the physical state of the block is changed very little. Only its position and velocity are altered. The body undergoes a *mechanical* change of state.

If the temperature of the block is raised, the ensuing alteration of the temperature and density of the body constitute a deeper-seated change of its physical state. The body undergoes a *thermal* change of state.

If the block is melted, and the resulting liquid is evaporated, the physical state of the body is yet more profoundly modified. The new state resembles the initial state very little. Yet the body is still regarded as being a mass of the same 'substance,' water; it has undergone changes of its *state of aggregation.*

If the block, finally, is converted into a mixture of hydrogen and oxygen gases, its physical properties are altered very deeply indeed. It is no longer regarded as being the same 'substance.' Its physical character is changed in almost every respect save in that of its mass. The body has undergone a *chemical* change of state.

Mechanical processes

Changes of the velocities and states of strain of bodies are termed mechanical processes. Of all changes of the physical states of bodies, the mechanical processes are among the most strikingly obvious, and are the least deep-seated. Because of their relatively simple character, comprehension of the way in which mechanical processes occur has been attained earlier and more comprehensively than has been the case in the study of any other class of changes of the physical states of bodies. At all times since the earliest recognition of mechanical laws, mechanics has been the highest developed branch of physical science.

Quantitative description of mechanical processes employs the principle of the conservation of mechanical energy. The mechanical work requisite to establish a state of strain

of a body is stored as the 'potential energy' of the body. The work requisite to impart a given velocity to a body is stored as the 'kinetic energy' of the body. And in any purely mechanical process the sum of the potential and kinetic energies of the participating bodies remains constant. The process may be, for example, the swinging of a pendulum in a vacuum, the movements of a mechanism driven by a falling weight, or the motions of the bodies constituting the solar system. In any case, the total mechanical energy of all the bodies participating in the process remains constant.

Supplementary changes of state

That the change of the state of a body is often connected with a change of the state of another body is an observation of fundamental significance in the study of physical processes. The falling of a clock weight is associated with the concurrent change of state of the mechanism of the clock; the cooling of a hot block of metal is associated with the heating of a contiguous cold block; the change of state of exploding gunpowder in a rifle is associated with an ensuing change of state of the bullet and a heating of the rifle barrel.

At the outset of any careful study of such mutually supplementary changes of the states of bodies, it is necessary to establish suitable definitions of the terms to be employed. We require at this stage to make definite what shall be understood by the terms 'body,' 'state,' 'change of state,' and 'supplementary change of state.'

Any material object or assemblage of objects, when no portion of it is removed and no extraneous matter is added to it, shall be termed a **body.** We may say that a body is an object, the masses of whose independently variable component substances remain unvaried. A mass of air, a quantity of brine together with an overlying layer of water vapor, and any closed receptacle together with its contents, are bodies. During the process of heating coexistent brine and vapor contained in a closed receptacle, the layer of brine is not a body; for a portion of this object is removed in the

concurrent evaporation. Unit mass of a mixture of alcohol and water of varying composition is not a body; for the masses of the independently variable component substances of this object do not remain unvaried.

When a body is participating in no physical process—when its physical character undergoes no alteration—the body shall be said to be in a quiescent **state.** Further, by the 'state' of a body shall always be understood a quiescent state. This convention will be found to save many words. In the present discussion, the meaning of the term 'state' shall not be broadened to include either what might be called a 'steady state,' as that of a disc rotating about an axis under the action of constant forces, or what might be called a 'turbulent state,' as that of an exploding mass of gunpowder, or as that of a mass of water in which currents are moving and differences of temperature are being equalized.

When a body passes, in any way, from any given state to any other state, it shall be said to undergo a **change of state.** And this change shall be considered to be the same 'change of state,' whatever the manner in which the process occurs. Thus a quiescent mixture of hydrogen and oxygen gases at a given pressure and temperature may be exploded, and the resulting water be brought to a quiescent state at an assigned pressure and temperature; or the mixture may first be cooled to the temperature of melting ice, and then exploded and brought to the assigned final state. In both cases the body concerned undergoes the same 'change of state.'

When a body undergoes a change of state in different ways, it shall be said that the **path** of the change of state is different in the different cases. The path of an actual change of state is the actual succession of 'non-quiescent states.' A continuous succession of quiescent states is a mathematical notion, and is termed a **reversible path.**

With reference to a given physical process, the assemblage of all the bodies participating in the process shall be termed the **isolated** body. A change of the state of an isolated

body may or may not involve changes of the state of more than one body. If the isolated body is a mass of gas, and its change of state is an abrupt expansion into an exhausted space, only one body is concerned in the process. But suppose the isolated body to be the mass of gas, together with a cylinder and heavy piston confining the gas; and the change of state to be an expansion of the gas together with a rise of the piston and a cooling of all the three bodies involved—the gas, the cylinder, and the piston. Here the change of state of the isolated body may be considered to consist of changes of the states of these three bodies; or we may regard it as consisting of the change of state of any one of the three, together with the change of state of the body composed of the assemblage of the other two.

Whenever, as in this illustration, a change of the state of an isolated body can be regarded as consisting of changes of the states of two bodies, each of these two changes of state shall be said to *supplement* the other. With reference to any given change of the state of any body, the **supplementary change of state** is the associated change of the state of the body composed of all the other bodies in any way participating in the process.

Nothing that has here been adduced entitles us to assume that a given change of state can always be associated with the same supplementary change of state. If a change of state A occurring on the path a is supplemented by a change of state B occurring on the path b, we are not at liberty to assume that the change A occurring on another path α can be supplemented by the change B occurring on any path whatsoever.

Mechanical aspects of changes of state

Many, possibly all, actually occurring physical processes present a mechanical side. A rise of temperature, for example, results from friction in a mechanism; electric effects follow the application of mechanical power to a dynamo; an excited electromagnet lifts a mass of iron; expanding steam drives a locomotive; exploding gunpowder imparts motion

to a bullet; the electrochemical action of a voltaic cell rings a doorbell. Because the mechanical aspect of a physical process is the aspect that we can most readily formulate in a quantitative way, we are led to seek a quantitative formulation of non-mechanical and of partly-mechanical processes through examination of the relations that these processes bear to mechanical changes of state.

In the development of this idea, a general observation of fundamental importance is that many non-mechanical or partly-mechanical changes of state either are or can be *supplemented* by mechanical operations. There are two distinguishable ways in which such processes can be thus supplemented:

I. **Directly,** without intervention of any intermediate change of state. As when the fall or rise of a heavy piston supplements the compression or expansion of a fluid—with a consequent change of the temperature and density of the fluid.

II. **Indirectly,** through shock or through intervention of friction. As when the temperature of a mass of liquid is raised by stirring it, or when through friction a block of metal is heated or a mass of ice is melted.

Many changes of state can indeed be indirectly supplemented by mechanical operations in other ways, as through intervention of electric or magnetic apparatus, or of radiation phenomenon. Such cases, however, shall for the present be omitted from consideration. In the following discussion, by 'indirectly supplemented' shall be invariably meant 'supplemented through intervention of friction,' the friction being understood to occur between solid rubbing surfaces, or between a solid body and a liquid that is stirred by it.

We shall now consider successively some typical cases in which changes of state can be brought into exclusive connection with mechanical operations. Five types of change are to be distinguished. In these, successively, a change of state:

(1) Is *directly* supplemented by a mechanical operation;
(2) Is or can be *indirectly* supplemented by a mechanical operation;
(3) Is not and cannot be supplemented, directly or indirectly, by a mechanical operation; but can be *replaced* by a mechanical operation acting through intervention of friction;
(4) Is *directly* supplemented in part by a mechanical operation; and for the rest is or can be *indirectly* supplemented by a mechanical operation;
(5) Is *directly* supplemented in part by a mechanical operation; and for the rest is not and cannot be supplemented, directly or indirectly, by a mechanical operation; but can be *replaced* by a mechanical operation acting through intervention of friction.

We shall now proceed to examine, in order, these five types of changes of state that can be brought into connection with mechanical operations.

Case 1.—A change is directly supplemented by a mechanical operation

Suppose a mass of gas, or coexistent masses of a liquid and its vapor, in a quiescent state in a vertical cylinder under a heavy piston capable of motion without friction. If the pressure exerted by the elastic fluid is not counterbalanced by the weight of the piston, a compression or expansion of the fluid will ensue, and this change of state may be supposed supplemented by the concurrent change of the level of the piston. In this case, the change of the state of the fluid is supplemented by a mechanical operation. The change of state of the fluid involves an alteration of density and temperature, and possibly a partial evaporation or condensation. In the supplementary change of state, the piston loses or gains a definite quantity of mechanical energy. This state of affairs shall be described by saying that the positive or negative quantity of mechanical energy developed by the piston is added to the fluid. In general:

DEF. *When a change of the state of a body is directly supplemented by a mechanical operation, the positive or negative mechanical energy developed in the mechanical operation is the* **quantity of mechanical energy added** *to the body.*

We leave open the question whether the quantity of mechanical energy added depends either on the path of the change of state or on the nature of the supplementary change of state.

If, in the illustration, the mechanical operation is a decrease of the level of the piston, the mechanical energy of the piston at any moment will be the sum of the potential and kinetic energies of this body. If it be supposed that the piston comes to rest after four oscillations (due to the inertia of the mass), the relation between the potential energy, the

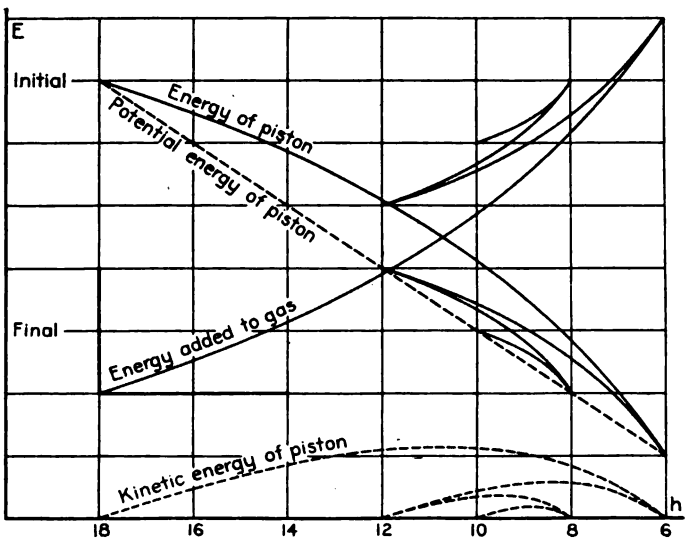

Fig. 1

kinetic energy, and the total energy of the piston, and the mechanical energy added to the fluid, will be somewhat as represented in the accompanying diagram. The fall of the piston of weight w from the height $h = 18$ to the height $h = 10$ results in addition of the mechanical energy $w(18-10)$ to the fluid.

Case 2.—A change is or can be indirectly supplemented by a mechanical operation

In the absence of a supplementary change, a mass of potassium sulphocyanate dissolving in a mass of water will attain a temperature below the initial temperature of the two-component body. Suppose occurring at constant volume, or practically so, a rise of the temperature of a block of metal, the fusion of a solid body, the evaporation of a liquid one, or the dissolving of a mass of potassium sulphocyanate in a mass of water under the condition that the initial and final temperatures of the body shall be the same. Each of these changes of state can be supplemented by an isometric[1] fall of the temperature of another body, or indeed by any one of a variety of changes of state. Also each of these changes can be supplemented by a mechanical operation acting through intervention of friction, can be 'indirectly supplemented' by a mechanical operation. The mechanical operation will develop a positive quantity of mechanical energy. This state of affairs shall be described by saying that the energy developed in the mechanical operation is added to the body undergoing the supplemented change of state. And the form of description shall be that prescribed by the following definitions.

DEF. *When a change of the state of a body is indirectly supplemented by a mechanical operation, the mechanical energy developed in the mechanical operation is the* **quantity of mechanical energy added** *to the body.*

DEF. *When a change of the state of a body is not, but can be, indirectly supplemented by a mechanical operation, the mechanical energy developed in the mechanical operation is the* **quantity of heat added** *to the body.*

The idea of a 'quantity of heat,' as here introduced, is not to be understood in any sense other than that specified in the definition. Especially is no hypothetical interpretation to be given to it. It is not to be interpreted as a quantity

[1] At constant volume.

of an imponderable fluid, or as a quantity of kinetic energy of hypothetical particles, or as *any* concept other than that presented by the definition. And we leave open the question whether the quantity of heat added depends either on the path of the change of state or on the nature of the supplementary change of state.

Case 3. A change is not and cannot be supplemented, directly or indirectly, by a mechanical operation; but it can be **replaced** *by a mechanical operation acting through intervention of friction*

In the absence of a supplementary change, a mass of sulphuric acid, H_2SO_4, dissolving in a mass of water will attain a temperature above the initial temperature of the two-component body. A chemical reaction in which, in absence of a supplementary change, the changing body attains a temperature above its initial temperature is an 'exothermal' reaction. Suppose occurring at constant volume, or practically so, a fall of the temperature of a block of metal, the solidification of a mass of liquid, the condensation of a mass of vapor, the mixing of a mass of sulphuric acid with a mass of water under the condition that the initial and final temperatures of the body shall be the same, or any exothermal reaction occurring subject to this condition. Each of these changes of state can be supplemented by an isometric rise of the temperature of another body, or indeed by any one of a variety of operations. No one of these changes of state can be supplemented by a mechanical operation, either directly or indirectly; but the actual rise of temperature or other operation that *does* supplement it can in every case be indirectly supplemented by a mechanical operation. In other words, the change itself can be *replaced* by a mechanical operation acting through intervention of friction. This mechanical operation will develop a positive quantity of mechanical energy. This state of affairs shall be described by saying that the energy developed in the mechanical operation is the quantity of energy developed in the

change of state that the mechanical operation can replace. And the form of description shall be that prescribed by the following definition:

DEF. *When a change of the state of a body can be replaced by a mechanical operation acting through intervention of friction, the mechanical energy developed in the mechanical operation is the* **quantity of heat developed** *by the body. The negative of this quantity is the 'quantity of heat added' to the body.*

We leave open the question whether the quantity of mechanical energy developed in the mechanical operation depends either on the path of the replaced change of state or on the nature of the supplementary change of state.

Cases 4, 5.—A change of state is or can be directly supplemented in part by a mechanical operation; and for the rest can be **indirectly** *supplemented by a mechanical operation, or can be* **replaced** *by a mechanical operation acting through intervention of friction*

Under a heavy piston a mass of gas or a mass of coexistent liquid and vapor is confined in a vertical cylinder standing on a hot block of metal. The fluid expands under the constant pressure of the piston. This change of state is supplemented in part by the mechanical operation of the piston, and for the rest (due to the cooling of the block) it can be indirectly supplemented by a mechanical operation. Again, a block of ice having the volume V_2 is contained in an open vessel standing on a hot block. When the ice is melted, its volume is $V_1 < V_2$. The change of state is supplemented in part by the mechanical action of the atmosphere, which adds to the water the mechanical work $p(V_2 - V_1)$, where p is the atmospheric pressure; and for the rest the change can be indirectly supplemented by a mechanical operation. If in each of these cases the hot block should be replaced by a sufficiently cold one, the change of state would be reversed. The fluid would contract under a constant pressure, and the liquid water would solidify under the pres-

sure of the atmosphere. In each case, the change of state would be supplemented in part by a mechanical action, and for the rest (in effecting the heating of the block) it could be *replaced* by a mechanical operation acting through intervention of friction. A similar state of affairs would obtain in the case of an exothermal chemical reaction involving any mechanical effect.

In an attempt to extend to such cases the ideas of additions of quantities of mechanical energy and of heat, we may for the moment confine our attention to a thoroughly typical case. In a horizontal cylinder, two masses of gas, A and B, are separated by a light, rigid, thermally conducting piston capable of motion with negligible friction. The two masses have the same initial temperature, but different initial pressures, $p_a > p_b$. The gas A expands and cools; the gas B is compressed and its temperature rises. Spontaneous equalization of these temperatures increases the pressure of A and decreases that of B, thus extending the process.

When the process is completed, A has developed a quantity of mechanical energy M, which may be regarded as having been transferred to B. For the actually occurring change of volume of A can be supposed replaced, in so far as the influence of this change of volume upon B is concerned, by the change of state of a mechanism acting upon the piston. The change of state of the gas A is supplemented by a change of state (that of the gas B), whose action is in part that of a mechanical operation absorbing the mechanical energy M, and whose action for the rest is that of a mechanical operation acting through intervention of friction. The (negative) quantity of mechanical energy developed by B shall be termed the *quantity of mechanical energy* developed by B and added to A; and the mechanical energy developed by the mechanical operation acting through intervention of friction shall be termed the *quantity of heat* developed by B and added to A.

The general case

The statements and definitions of this detailed examina-

tion of the mechanical aspects of changes of the physical state of bodies may now be summarized, as follows:

STMT. *Many supplemented changes of the physical states of bodies can be brought directly or indirectly, or both directly and indirectly, into exclusive connection with mechanical operations. Every such change of state is directly supplemented, wholly or in part or not at all, by a mechanical operation; and, in so far as it is not so supplemented, it either is or can be supplemented by a mechanical operation acting through intervention of friction, or it can be replaced by a mechanical operation acting through intervention of friction.*

DEF. *When two bodies undergo mutually supplementary changes of state of the class described, the quantity of mechanical energy developed by either one of the bodies is the* **quantity of mechanical energy added** *to the other.*

And the mechanical energy developed in the mechanical operation that can for the rest supplement one of the changes of state and replace the other, on the actual paths of these changes of state, is the **quantity of heat added** *to the body undergoing the supplemented change of state, and is the negative of the quantity of heat added to the body undergoing the replaced change of state.*

In the establishment of these definitions we leave open the question whether the quantities of mechanical energy and of heat added to a body in a change of its state depend either on the path of the change of state or on the nature of the supplementary change of state. It is readily seen, however, that *in general* these quantities are certainly not independent of the *path* of the change of state. This may be shown by an example. The state of a given mass of coexistent liquid and vapor is determined by the volume V and the temperature τ of the mass. Under the constant pressure determined by the initial state, let the state change from V_a, τ to V_b, τ where $V_b > V_a$. The body develops a quantity of mechanical energy M_1, and absorbs a quantity of heat Q_1. Again, let the body pass from its initial state to a state in which its volume is V_b, by abrupt expansion into an adjoining vacuum $V_b - V_a$.

The temperature will fall thereby, whereupon the state V_b, τ can be reached on addition of a quantity of heat Q_2. On the first of these two paths the quantity of mechanical energy M_1 is added to the body; on the second path the mechanical energy added is zero. And it can be experimentally shown that the quantities of heat Q_1, Q_2 are not equal.

Thermodynamic changes of state

The present discussion is concerned with supplemented changes of state, not purely mechanical, that can be brought directly or indirectly or both directly and indirectly into connection with mechanical operations. The states of any given body, attainable through changes of state of this class, constitute the continuous assemblage of the **thermodynamic states** of the body. All such changes of state, and also all possible changes of the state of any *isolated* body from one thermodynamic state to another, are termed **thermodynamic changes of state.** The study of thermodynamic changes of state is **thermodynamics.**

Many changes of the physical states of bodies can be supplemented or replaced in part by mechanical operations acting through intervention of friction, and in part by mechanical operations acting indirectly in other ways, as through intervention of the action of electric or magnetic apparatus or of radiation. Such changes of state must indeed be regarded as included in the province of thermodynamics understood in a broad sense. But their study is an *extension* of the principles of thermodynamics to a domain lying beyond the immediate province of the subject, and it cannot conveniently be entered upon until after this immediate province has been surveyed.

Thermodynamic processes, like mechanical processes, are abstractions. In either case certain features of a process abstracted from the actual phenomena, constitute the subject of study. Purely thermodynamic operations, like purely mechanical operations, do not exist. A mechanical operation is complicated by unavoidable friction, or electrostatic at-

tractions, and the like; and a thermodynamic operation involves features of radiation and what not. In any case it is an ideal, abstract process that is the subject of study; but the disparity between it and the corresponding actual physical operation is kept as small as possible.

Summary of Part I.

Physical processes.—An ensemble of changes of the physical properties of an assemblage of bodies is a 'physical process.' Physical processes may be classified in accordance with the degree in which the physical character of the participating bodies is modified. Of all physical happenings, the mechanical processes are the *least* deep-seated. The way in which they occur is better understood than is the way in which any other physical processes occur. In any purely mechanical process the sum of the potential and kinetic energies of the participating bodies remains constant.

Supplementary changes of state.—A *body* is an object, the masses of whose independently variable component substances remain unvaried. When the physical character of a body undergoes no alteration, the body is said to be in a (quiescent) physical *state*. When the body passes from one state to another it undergoes a definite *change of state*. The *path* of an actual change of state is the actual succession of 'non-quiescent states.' A continuous succession of quiescent states is a mathematical notion, and is termed a *reversible path*. With reference to any given change of the physical state of any body, the *supplementary change of state* is the associated change of state of the body composed of all the other bodies in any way participating in the process. It may not be assumed that a given change of state can always be associated with the same supplementary change of state.

Mechanical aspects of changes of state.—Many supplemented changes of the physical states of bodies can be brought 'directly' (without intervention of an intermediate change of state), or 'indirectly' (through intervention of

friction), or both directly and indirectly, into exclusive connection with mechanical operations. Every such change of state is directly supplemented, wholly or in part or not at all, by a mechanical operation; and, in so far as it is not so supplemented, it either is or can be supplemented by a mechanical operation acting through intervention of friction, or it can be replaced by a mechanical operation acting through intervention of friction.

DEF. When two bodies undergo mutually supplementary changes of state of the class described, the quantity of mechanical energy developed by either one of the bodies is the *quantity of mechanical energy added* to the other. And the mechanical energy developed in the mechanical operation that can for the rest supplement one of the changes of state and replace the other, on the actual paths of these changes of state, is the *quantity of heat added* to the body undergoing the supplemented change of state, and is the negative of the quantity of heat added to the body undergoing the replaced change of state.

In general, the quantities of mechanical energy and of heat added to a body in a change of its state are not independent of the path of the change of state.

Thermodynamic changes of state.—The present study is concerned with supplemented changes of state, not purely mechanical, that can be brought directly or indirectly or both directly and indirectly into connection with mechanical operations. The states of any given body, attainable through such changes of state, constitute the continuous assemblage of the *thermodynamic states* of the body. All such changes of state, and also all possible changes of the state of any *isolated* body from one thermodynamic state to another, are termed *thermodynamic changes of state.* The study of thermodynamic changes of state is *thermodynamics.* As here defined, thermodynamic changes of state are abstractions.

PART II. THE FIRST LAW OF THERMODYNAMICS

The problem

The conclusion of the foregoing discussion may be stated

to be that all thermodynamic changes of state can be brought into exclusive connection with operations of a wholly mechanical character, that all such changes can be supplemented or replaced—or both supplemented and replaced—by mechanical operations.

As has been stated, we seek to attain a quantitative formulation of thermodynamic changes of state through examination of the relations that these operations bear to mechanical changes of state.

In purely mechanical processes, the total mechanical energy of the participating bodies remains constant. This fact offers a promising suggestion. It leads us to enquire whether a physical quantity, the 'energy of a body,' can be defined in such a way that the total energy of the bodies participating in any thermodynamic process will remain constant. We shall now consider this question.

If it can be shown that the 'energy of a body,' thus established by definition, is uniquely determined by the state of the body; and if then the energies of the bodies participating in a thermodynamic process can be analytically expressed by means of independent measurable physical quantities determined by the thermodynamic states of the bodies; we shall thereby obtain analytical *relations* between such physical variables. These relations will quantitatively describe the thermodynamic changes of state of the bodies. They will thus constitute, at least in some measure, a *rational theory* of thermodynamics.

A definition

If it is possible to define the 'energy of a body' in such a way that the sum of the energies of the bodies participating in any thermodynamic process remains constant, the 'change of the energy' of a body undergoing a change of thermodynamic state must be defined in such a way that:

(*a*) If the change of state is or can be supplemented, directly or indirectly or both directly and indirectly, by mechanical operations, the change of the energy of the body

and the total change of the mechanical energies of the bodies executing the mechanical operations must be equal and have opposite signs. *I. e.*, the change of the energy of the body must be equal to the algebraic sum of the quantities of mechanical energy and of heat added to the body.

(*b*) The changes of the energies of two bodies undergoing mutually supplementary changes of thermodynamic state must be equal and have opposite signs. *I. e.*, the change of the energy of a body undergoing *any* supplemented change of thermodynamic state must be equal to the algebraic sum of the quantities of mechanical energy and of heat added to the body.

(*c*) The change of the energy of any isolated body undergoing a change of thermodynamic state must be zero—whether the change of state does or does not consist of mutually supplementary changes of state.

In short, if the 'energy of a body' *can be* defined in such a way that the sum of the energies of the bodies participating in any thermodynamic process will remain constant, it must be defined by means of its *changes*, and in the following fashion:

DEF. The **change of the energy,** U_{ab}, of a body undergoing a change of thermodynamic state from the state a to the state b is equal to the algebraic sum of the quantities of mechanical energy M_{ab} and heat Q_{ab} added to the body in the course of its change of state,

$$U_{ab} = M_{ab} + Q_{ab}.$$

Necessary conditions

It is now to be enquired whether any 'change of the energy' of a body is the change of a quantity $E_x + E_o$ whose value, save for an additive constant E_o, is uniquely determined by the thermodynamic state x of the body; whether

$$(1) \qquad U_{ab} = (E_x + E_o)\Big|_a^b = E_b - E_a.$$

We proceed to examine the conditions that must be fulfilled in order that the relation (1) shall be satisfied.

It must first be shown that given transfers of mechanical energy and of heat are definite quantities. It must be shown that in any recurrence, on a given path, of a thermodynamic process consisting of given mutually supplementary changes of the states of bodies, the quantity of mechanical energy transferred from one body to the other is always the same, and the quantity of heat transferred from one body to the other is always the same. If it should be shown that these conditions are fulfilled, it would be shown that the change of the energy, U_{ab}, of a body has always the same value when the change of thermodynamic state *ab* occurs on a given path with a given supplementary change of state.

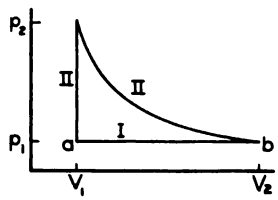

Fig. 2

Yet the change of energy U_{ab} might vary with the *path* of the change of state. Suppose a mass of gas, whose thermodynamic state is determined by its pressure p and volume V, confined under a piston in a vertical cylinder resting on a metal block. Let the mass change from the state $a = p_1$, V_1 to the state $b = p_1, V_2$; this change of state being supplemented by a cooling of the block through the temperature interval $\tau_2 - \tau_1$, together with a rise of the piston through the increment of height $h_2 - h_1$. On this 'path I,' the change of energy U_{ab} of the gas is the algebraic sum of the negative mechanical energy developed by the piston and the positive heat developed by the block. On a 'path II,' let the gas change from its initial state to the state p_2, V_1; the change being supplemented by a cooling of the block of metal through the temperature interval $\tau_2 - \tau_1'$; whereupon ensues a concluding change (adiabatic expansion) to the state p_1, V_2, supplemented by a rise of the piston through the increment

of height $h_2 - h_1$. Will it be observed that $\tau_1 = \tau_1'$? For these temperatures must be the same if the quantity U_{ab} have the same value with reference to both paths.

If it should be shown that U_{ab} *is*, in general, independent of the path of the change of state, this quantity might yet vary with the *supplementary change* of state. For example, in the above illustration, let the change of state of the gas, occurring on the path 1, be supplemented by a rise of the piston from h_1 to h_2, together with a mixing of certain quantities of sulphuric acid and water, the initial and final temperatures of this body being the final temperature of the gas. Will it be observed that the quantity of mechanical energy expended, through intervention of friction, to replace the mixing, is equal to that requisite to replace the cooling of the block from τ_2 to τ_1? For these quantities of mechanical energy must be equal, if the quantity U_{ab} is to have the same value in both cases.

Sufficiency of the conditions

If it should be shown to be true that the change of energy U_{ab} of a body undergoing any change of thermodynamic state *ab* is independent of the path of the change of state, and is independent of the supplementary change of state, it would thereby be shown that the quantity U_{ab} is uniquely determined by the end states of the body. And it would follow that the change of energy U_{ab} is equal to the concurrent change of the value of a quantity $E_x + E_o$ determined by the thermodynamic state x of the body and containing an arbitrary additive constant E_o. This statement may be established somewhat as follows.

It will first be observed that, if a, b, c, be any three states of a body, we shall have

$$U_{ab} = M_{ab} + Q_{ab}$$
$$U_{bc} = M_{bc} + Q_{bc};$$

whence

$$U_{ab} + U_{bc} = (M_{ab} + M_{bc}) + (Q_{ab} + Q_{bc}).$$

The second member of this equation, being the total mechanical energy and the total heat absorbed in any two consecutive paths *ab*, *bc*, is the change of the energy U_{ac} of the body undergoing the change of state from *a* to *c*. Therefore, generally,

$$U_{ab} + U_{bc} = U_{ac}.$$

Now it may be that the ensemble of the realizable states of a body is an assemblage of contiguous regions of states, in each of which the quantities M_{ab} and Q_{ab} change in value at continuous rates as the physical variables determining the state are varied on any reversible path. Thus, in the region of states in which the body consists of a homogeneous mass of vapor, or in the region in which it consists of coexisting masses of liquid and vapor, the quantities M_{ab} and Q_{ab} change in value, with varying *b*, at continuous rates during any reversible process. But the rates are discontinuous when the body passes from one region to the other. Let the reversible process be an isothermal compression. In compression of the vapor from the state 1, the mechanical energy added is the work

$$-\int_1^V p(V)dV;$$

where the continuous function $p(V)$ is the pressure supported by the body at states on the isotherm. In compression of

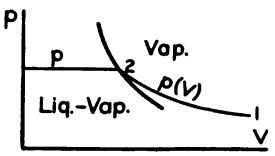

Fig. 3

the coexisting liquid and vapor from the state 2, the mechanical energy added is the work

$$-\int_2^V p dV;$$

where p is the constant vapor pressure of the body. At the point 2, the rate of addition of mechanical energy, per unit change of volume, changes discontinuously from the variable value $p(V)$ to the constant value p.

Within any region in which M_{ab} and Q_{ab} change at continuous rates, let o be any fixed state of reference and let a,b be any assigned states. Within this region, the states of the body are determined by the values of certain independent measurable physical variables. Let α denote the values of these variables at a, and β the values at b. Then the change of energy U_{oa} is determined by the values α,

$$U_{oa} = u(\alpha). \tag{1}$$

Again, $U_{oa} + U_{ab}$ is equal to U_{ob}, and so is determined in the same way by the values β,

$$U_{oa} + U_{ab} = u(\beta). \tag{2}$$

Subtracting 1 from 2,

$$U_{ab} = u(\beta) - u(\alpha).$$

I. e., the change of energy U_{ab} is equal to the concurrent change of a quantity uniquely determined by the state of the body. And this quantity may contain an arbitrary additive constant E_o, so that we have

$$\begin{aligned} u(\xi) &= E_x + E_o \\ U_{ab} &= (E_x + E_o)\Big|_a^b. \end{aligned}$$

Suppose, now, that the states a and b lie in contiguous regions of state. Then, if the path ab crosses the boundary

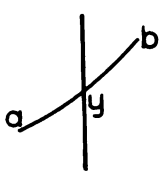

Fig. 4

at the state y, and if η denotes the values of the state-variables at y, we shall have

$$\begin{aligned} U_{ab} &= U_{ay} + U_{yb} \\ &= \Big(u(\eta) - u(\alpha)\Big) + \Big(w(\beta) - w(\eta)\Big). \end{aligned}$$

But U_{ab} is independent of the state y, *i. e.*, of the values η, and is determined by α, β. So

$$u(\eta) - w(\eta) = 0,$$

wherefore

$$U_{ab} = w(\beta) - u(\alpha).$$

The conclusion attained is as follows: If it should be shown, by experimental means, that the algebraic sum

$$U_{ab} = M_{ab} + Q_{ab}$$

of the mechanical energy and heat added to any body, when the body passes from any thermodynamic state a to any other thermodynamic state b, is independent of the supplementary change of state and of the path of the change of state, it would follow that the 'change of energy'

$$U_{ab} = M_{ab} + Q_{ab}$$

is equal to the concurrent change of the value of a quantity E uniquely determined by the thermodynamic state of the body; though this quantity may be determined in different ways in different regions of state. And the quantity E can contain an arbitrary additive constant,

$$E = E_x + E_o.$$

So we have, in general,

$$\begin{aligned} U_{ab} &= (E_x + E_o)\Big|_a^b \\ E_b - E_a &= M_{ab} + Q_{ab}. \end{aligned}$$

The first law of thermodynamics

In the experimental study of thermodynamic processes, there have been made very extended and careful measurements of the quantities of mechanical energy and of heat transferred between bodies undergoing mutually supplementary changes of state. In some experiments, mechanical operations have supplemented changes of the temperatures

of bodies, and changes of their states of aggregation. In other experiments, conducted in 'calorimeters', changes of temperature, changes of states of aggregation, the formation of homogeneous liquid mixtures from separate liquids or from liquids and solids, chemical changes of state, and combinations of these, have supplemented changes of the temperatures of other bodies, and sometimes mechanical actions as well. The results obtained in an immense number of such experiments give extensive support to the hypothesis that the algebraic sum of the mechanical energy and heat added to a body in any change of its thermodynamic state is independent of the supplementary change of state and of the path of the change of state.

These results therefore lead to the conclusion that:

The algebraic sum of the mechanical energy and heat added to a body in any change of its thermodynamic state is equal to the concurrent change of the value of a quantity, determined, it may be in different ways in different regions of state, but continuous and one-valued in any region, and containing an arbitrary additive constant,

$$\begin{aligned} M_{ab} + Q_{ab} &= (E_x + E_o)\Big|_a^b \\ &= E_b - E_a. \end{aligned}$$

This hypothesis is the **first law of thermodynamics.** The quantity $E_x + E_o$ is the *energy* of the body. Unless otherwise stated, the 'energy' of a body shall hereafter be understood in this sense. The quantity $E_x + E_o$ is sometimes termed the 'inner energy' of the body, to distinguish it from the kinetic and potential energies, whose sum is the mechanical energy of the body, or from the energy due to an electrostatic charge or to other actions. The justification of the first law of thermodynamics lies largely in the agreement of its consequences with experience. This agreement is very extended and exact.

The law involves the statement that the algebraic sum of the changes of the energies of bodies undergoing mutually supplementary thermodynamic changes of state is zero;

or, more generally, that the energy of an isolated body undergoing any change of thermodynamic state is constant. This form of statement is the **law of the conservation of energy,** as applied to thermodynamic processes.

The calory

The numerical value of a quantity of heat transferred from one body to another is determined by the quantity of mechanical energy developed in a mechanical operation. This mechanical operation can supplement a rise of the temperature of a body of water. The mass of the body of water whose temperature is thus raised through a fixed interval $\tau - \tau_r$ is proportional to the quantity of mechanical energy developed in the mechanical operation. So this mass is an expression of the quantity of heat transferred from the one body to the other. The heat-unit determined by the quantity of mechanical energy requisite to raise unit mass of water through the interval $\tau - \tau_r = 1$, from an assigned temperature τ_r (usually 15° C.) on a given scale of temperatures, is termed the **calory.** The calory is practically identical with the 'specific heat' of water at the assigned temperature; though, strictly, the specific heat of a substance is the quantity of heat absorbed, by unit mass of the substance, *per* unit increase of the temperature of the mass. Strictly, the specific heat of a substance is defined with reference to a given path, and is a *rate.* When expressed in mechanical units, the calory is often termed the **mechanical equivalent of heat.**

Scholium

In considering transfers of heat, it is well to bear in mind that positively "adding heat" to a body—"heating the body"—is not in general associated with a rise of the temperature of the body. When heat is added to a block of metal, the temperature of the block rises. When heat is added to a mass of liquid water and overlying water vapor supporting a constant pressure, the temperature of the mass is not altered. Heat may be added to a mass of potassium sulphocyanate

and water, in the process of forming a mixture, and the temperature falls. An addition of heat to a body involves a change of the state of the body, but it may not involve a change of the temperature alone, and it may not involve a change of the temperature at all. Contrariwise, a change of the temperature of a body does not necessarily involve absorption or development of heat. When a mass of air is adiabatically[1] compressed, or when it expands into a vacuum, the temperature of the mass changes, but no heat is added to it.

Summary of Part II.

The fundamental problem.—The thesis of Part I is that all thermodynamic changes of state can be supplemented or replaced—or both supplemented and replaced—by mechanical operations. We seek to establish a quantitative formulation of thermodynamic changes of state through examination of the relations that these operations bear to mechanical changes of state. Can this end be attained through defining the 'energy of a body' in such a way that the total energy of the bodies participating in any thermodynamic process will remain constant? So defined:

DEF. The energy of a body in any thermodynamic state x is a quantity $E_x + E_o$, whose change U_{ab} when the body undergoes a change of thermodynamic state from the state a to the state b is equal to the algebraic sum of the quantities of mechanical energy M_{ab} and heat Q_{ab} added to the body in the course of its change of state,

$$U_{ab} = M_{ab} + Q_{ab}.$$

It remains to be determined whether the quantity U_{ab} is really equal to the change of a quantity $E_x + E_o$ whose value, save for an arbitrary additive constant E_o, is uniquely determined by the thermodynamic state x of the body; whether

$$U_{ab} = (E_x + E_o)\Big|_a^b.$$

[1] Without transfer of heat to or from the mass.

To establish that U_{ab} is equal to the change of such a quantity, it is necessary to establish that U_{ab} is determined by the states a,b; it is necessary to establish that U_{ab} is independent of the path of the change of state ab, and of the supplementary change of state.

The necessary condition, that U_{ab} is determined by the states a,b is also the sufficient condition. For, if this condition is fulfilled, with regard to any paths oa, ab we shall have

$$U_{oa} = M_{oa} + Q_{oa}$$
$$U_{ab} = M_{ab} + Q_{ab};$$

whence,

$$U_{oa} + U_{ab} = (M_{oa} + M_{ab}) + (Q_{oa} + Q_{ab})$$
$$= U_{ob}.$$

Hence,

$$U_{ab} = U_{ob} - U_{oa}.$$

Taking the state o as a fixed state of reference, U_{ob} is determined by the state b, and U_{oa} by the state a. So U_{ab} is equal to a quantity determined by b, less a quantity determined by a. It follows that U_{ab} is equal to the concurrent change of the value of a quantity $E_x + E_o$ uniquely determined by the thermodynamic state of the body; though E_x may be determined in different ways in different contiguous regions of state.

The first law.—Extended and careful experimental study has been made of thermodynamic processes in which mechanical operations supplement changes of the temperatures and changes of the states of aggregation of bodies, and of processes in which various changes of thermodynamic state supplement changes of the temperatures of other bodies and often mechanical actions as well. The results obtained in an immense number of such experiments give extensive support to the hypothesis that the algebraic sum of the mechanical energy and heat added to a body in any change of its thermodynamic state is independent of the supple-

mentary change of state, and of the path of the change of state.

These results therefore lead to the conclusion that: The algebraic sum of the mechanical energy and heat added to a body in any change of its thermodynamic state is equal to the concurrent change of the value of a quantity, determined it may be in different ways in different regions of state, but continuous and one-valued in any region, and containing an arbitrary additive constant,

$$\begin{aligned} M_{ab} + Q_{ab} &= (E_x + E_o)\Big|_a^b \\ &= E_b - E_a. \end{aligned}$$

This conclusion is the **first law of thermodynamics.** The quantity $E_x + E_o$ is the **energy** of the body. The *justification* of the first law of thermodynamics lies largely in the extended and exact agreement of its consequences with experience.

The calory.—The heat unit determined by the quantity of mechanical energy requisite to raise unit mass of water through the interval $\tau - \tau_r = 1$ is termed the **calory.** The calory is practically identical with the specific heat of water at τ_r (usually 15° C.). When expressed in mechanical units it is known as the **mechanical equivalent of heat.**

THE VALIDITY OF FARADAY'S LAW AT LOW TEMPERATURES

BY WENDELL G. WILCOX

The importance of determining the range and validity of a law which is so fundamental as that of Faraday, and which is so closely linked with our present day conceptions and theories, is obvious. Faraday[1] himself investigated the influence of some of the conditions of electrolysis, showing that the size of the electrodes, the distance they were apart, the variations in the density of the current, the differences in the concentration of the solution undergoing electrolysis, and the nature of the solution (in the case of the hydrogen voltameter), had no influence on the electrochemical equivalent.

Various points in connection with the internal work of batteries were afterwards investigated by Grove,[2] Depretz,[3] Matteucci,[4] Renault,[5] and others. The accuracy and the improvement of the voltameter have been investigated by F. and W. Kohlrausch,[6] Lord Rayleigh,[7] T. W. Richards[8] and his pupils, and a number of other investigators.

The effect of temperature on the electrochemical equivalent was indirectly investigated by Faraday.[9] He showed that his law holds for the electrolysis of some of the fused salts of the heavy metals. Recently Richard Lorenz and A. Helfenstein[10] have confirmed his results, showing that Faraday's law holds for such temperatures as are attained in the

[1] Phil. Trans., 124, 85 (1834).

[2] Phil. Mag. [3], 23, 376 (1843).

[3] Comptes rendus, 33, 185 (1851).

[4] Ann. Chim. Phys. [2], 58, 78 (1835).

[5] Ibid. [4], 11, 137 (1867).

[6] Wied. Ann., 27, 1 (1886).

[7] Phil. Trans., 175, 458, 411 (1884).

[8] Zeit. phys. Chem., 32, 321 (1900); 41, 302 (1902); Jour. Am. Chem. Soc., 27, 232 (1905).

[9] Loc. cit.

[10] Zeit. anorg. Chem., 23, 97 (1900).

electrolysis of the fused chlorides of the heavy metals. Richards and Stull,[1] have obtained very good confirmation of the law by electrolyzing silver nitrate dissolved in a fused mixture of potassium and sodium nitrates.

The object of the present investigation is to extend these researches to low temperatures. A pyridine solution of silver nitrate was chosen for electrolysis at low temperatures, for this solution yields a firm, compact, white deposit, and the freezing point of the saturated solution is as low as —65° C.

The pyridine which was used was Merck's chemically pure. It was purified by distilling several times and drying over fused caustic potash and finally fractionating again. The fraction boiling at 115–6° at 742 mm was used. Kahlbaum's chemically pure silver nitrate previously fused was employed. Silver by Stas's method was cast into sticks in a graphite mold. The surface of these sticks was machined off and cleaned, and they were then used as anodes. The water used was carefully purified by the usual methods. The pyridine solution of silver nitrate was a 10 percent solution by weight. The aqueous solution was neutral and contained 10 per cent by weight of silver nitrate.

Two large platinum crucibles weighing 40 grams each served as voltameters. They were arranged in series, great care being taken to insure no leakage of current. The voltameter containing the pyridine solution of silver nitrate was kept at low temperatures by means of a cooling mixture placed in a thermostat. The voltameter containing the aqueous solution of silver nitrate was kept at about 20° C in all the experiments.

The method of determination was in brief as follows: The voltameters having been filled with their respective solutions, the current was turned on. At the close of the experiment, the solution was siphoned out of the crucible; the latter was filled with pure water and allowed to stand for several hours to leach out any occluded solution. The water

[1] Zeit. phys. Chem., **42**, 621 (1903).

was then siphoned off, and the crucibles washed with alcohol and with ether, and then heated to 155° C in the air bath for forty minutes, after which they were cooled in the desiccator and weighed. The anodes used were always covered with a fresh muslin jacket to prevent loose particles of silver from dropping into the crucible. The solutions were electrolyzed but once.

Before proceeding with the work at low temperatures, a few preliminary experiments were made at room temperatures, though Kahlenberg[1] has already shown that Faraday's law holds for non-aqueous solutions. The results obtained are as follows:

TABLE 1

No. of experiment	Time	Current density in milliamperes per sq. cm	Deposit from water solution gram	Deposit from pyridine solution gram
1	1 hr. 8 min.	1.0	0.2502	0.2506
2	1 hr. 31 min.	0.9	0.3212	0.3214
3	45 min.	0.9	0.1571	0.1572
4	1 hr.	1.0	0.2236	0.2239

The current density given here, as in the following tables, is the average. The current fluctuated somewhat. The effect of changing the temperature during the electrolysis was next tried. In each case the voltameter containing the pyridine solution was cooled down to the temperature indicated, and then brought back to room temperature while the current was flowing.

TABLE 2

No. of experiment	Time min	Current density in milliamperes per sq. cm	Deposit from water solution at 20° C gram	Deposit from pyridine solution gram	Temperature of pyridine solution
1	60	1.0	0.2013	0.2022	20° to — 1°
2	40	1.0	0.1458	0.1460	20° to — 5°
3	45	1.5	0.2212	0.2214	20° to — 8°
4	40	0.5	0.0789	0.0763	20° to —40°

[1] Jour. Phys. Chem., 4, 349 (1900).

The first three results show good concordance; the low result obtained for the pyridine deposit in the fourth experiment will be spoken of again in connection with the results obtained at temperatures as low as —30° or —40° C.

Experiments were next performed at temperatures ranging from 1° to —55°, keeping the temperature as constant as possible during the experiment. Preliminary tests showed that while it is comparatively easy to get fine white deposits from pyridine solution of silver nitrate at ordinary temperatures by using a current density of one milliampere per square cm, nevertheless at temperatures a little below zero, the deposit begins to be carbonaceous and as the temperature is further lowered, the difficulty of obtaining non-carbonaceous deposits increases enormously. The pyridine solution darkens at once on electrolyzing and the deposit remains dark, but clears up on washing and heating. Furthermore it was found that the deposit from the pyridine was always lighter than that from the aqueous solution. These things pointed to a decomposition of the pyridine under the existing conditions. Attempts were made to overcome this difficulty by lowering the current density; but although a current of only two-tenths of a milliampere per square cm was used, the same results were obtained although to a less degree. The anode was then flattened considerably so as to form a stirrer, and was rotated rapidly. Under these conditions the following results were obtained:

TABLE 3

No. of experiment	Deposit from water solution at 20° C gram	Deposit from pyridine solution gram	Temperature of pyridine solution
1	0.1069	0.1070	1°
2	0.1079	0.1079	—10°
3	0.1370	0.1368	—15°
4	0.1450	0.1445	—20°
5	0.1486	0.1451	—20°
6	0.1436	0.1416	—20°
7	0.1342	0.1432	—25°
8	0.0584	0.0570	—30°

TABLE 3—(*Continued*)

No. of experiment	Deposit from water solution at 20° C gram	Deposit from pyridine solution gram	Temperature of pyridine solution
9	0.0600	0.0589	—30°
10	0.1356	0.1327	—30°
11	0.0520	0.0474	—35°
12	0.0446	0.0362	—40°
13	0.0565	0.0509	—40°
14	0.0401	0.0364	—55°

In all of the above experiments the current density ranged from 0.2–0.5 milliamperes per sq. cm.

The results given above have been selected from a much larger number of those obtained as they show the general trend of the experiments. It is to be noticed that the discrepancies increase, the lower the temperature at which electrolysis takes place, and that such discrepancies are very roughly proportional to the weight of the deposit. That this discrepancy is due to decomposition of the pyridine, and that the difference in question increases with the increase of the change in concentration at the electrodes is shown by experiments 4, 5 and 6 in the above table. Five and six were purposely not stirred, while four was stirred vigorously, the result being a much better concordance in experiment four.

While the results do not agree exactly at low temperatures, they nevertheless appear to admit of the following conclusions:

(1) That the electrochemical equivalent is independent of temperature change during the course of the electrolysis.

(2) That Faraday's law holds for low temperatures provided secondary changes are taken into consideration.

In conclusion, the author desires to express his indebtedness to Professor Kahlenberg for the helpful advice and suggestions that he has given during the course of the work.

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THE NATURE OF THE CAST IRONS

BY G. B. UPTON

In a paper on "The Iron-Carbon Equilibrium"[1] I have discussed the history of the problem of the nature of the iron-carbon alloys, and have outlined a possible equilibrium diagram which is an extension of the familiar Roozeboom diagram. This new diagram is consistent with the cooling curve work of Carpenter and Keeling[2] and capable of explaining the structure and properties of the cast irons. In the present paper I desire to review the arguments of my first paper, extending largely the list of data considered. I will try to show that this new equilibrium diagram is in better harmony with the great mass of published research on iron-carbon relations than is the "metastable equilibrium" hypothesis. Then comes an explanation of the nature of the cast irons according to the new diagram.

The two diagrams in question are given in Figs. 1 and 2. Fig. 1 gives the double equilibrium diagram with details according to Benedicks. Similar diagrams in all essentials are given by Ruer, Heyn, LeChatelier, Charpy, and others. The French and German metallographists seem committed to the double equilibrium explanation of the iron-carbon relations, employing this explanation especially for the difficult case of the cast irons. They believe that we have to deal with (1) a stable equilibrium of iron and graphite, in which equilibrium at low temperatures no carbon whatever would remain dissolved in or combined with the iron; (2) a metastable equilibrium of iron and the iron carbide Fe_3C, called cementite. This metastable equilibrium is supposed to be obtained with any but the very slowest cooling of the melt, especially if the carbon content is high. Commercial irons then represent various mixtures and intergrades be-

[1] Jour. Phys. Chem., 12, 507 (1908).

[2] Iron and Steel Inst. Jour., 1904, i, 224; Iron and Steel Mag., 7, 628 (1904).

tween the "stable" and the "metastable" relations. Rather peculiarly the "stable" and "metastable" equilibria are made substantially coincident down to 800° C, below which temperature few or no changes occur in commercial cast irons. This totality of coincidence of stable and metastable equilibrium diagrams is hardly to be expected, and should certainly make a metallographist pause.

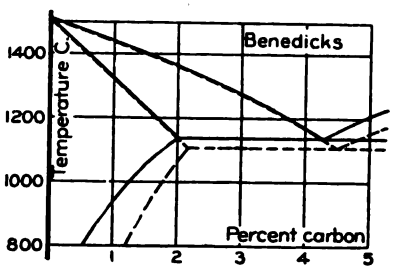

Fig. 1

Full lines, stable equilibrium of iron and graphite. Dotted lines, metastable equilibrium of iron and Fe_3C

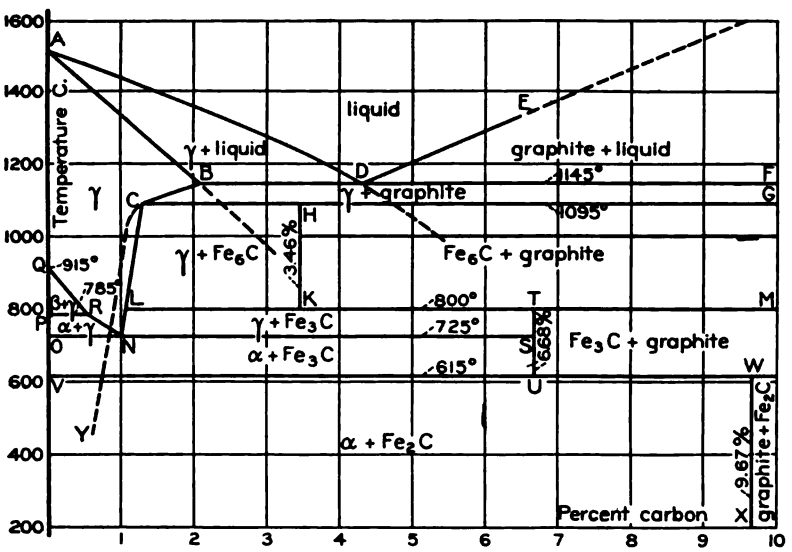

Fig. 2

Upton modification of the Roozeboom diagram.

Roozeboom based his diagram on the incomplete cooling curve work of Roberts-Austen, and from that had to make what he could. When Carpenter and Keeling took up the cooling curve study more carefully and completely they found evidence of two inversions which had been missed by Roberts-Austen. Had Roozeboom known of these new inversions he would most certainly have revised his diagram. Fig. 3 shows the inversion points determined by Carpenter and Keeling superposed on the Roozeboom diagram. The new

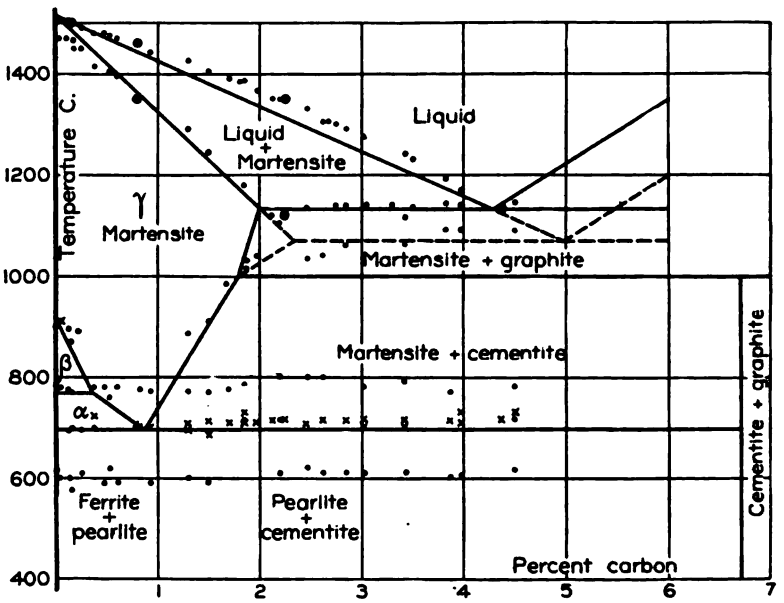

Fig. 3

inversions are found (1) at 800° beyond 1 percent carbon (2) at 600° across the diagram. It was in attempting to find place for these new inversions, and also simultaneously to interpret masses of other data, that I was led to propose the diagram shown in Fig. 2.

In this proposed diagram the liquidus and solidus lines are like the same lines of Fig. 1, and follow the temperature determinations of Carpenter and Keeling. Instead of a

double equilibrium, however, there comes below the line of the liquid eutectic a narrow field of graphite plus solid solution of carbon in γ iron. Below this again come fields of $\gamma + Fe_6C$ and Fe_6C + graphite. (γ as here used means the solid solution of carbon in γ iron). As to the Fe_6C, I should say that I have put it as a chemical compound for the sake of simplicity in the diagram. I do not insist that there is such a compound, for all the conditions I can impose would be equally well met by a narrow field of a second solid solution, with a limiting concentration of carbon around 3.5 percent. Parallel cases for such a second solution are furnished in the equilibrium diagrams of copper with zinc,[1] tin,[2] and aluminum.[3] Between 800° and 725° lies that field of $\gamma + Fe_3C$ which in Roozeboom's diagram was made to go (arbitrarily) to 1000°. At 600° $\alpha + Fe_3C$ is given as changing to $\alpha + Fe_2C$.

Before going farther I must make sure of my primary data, the 800° and 600° inversions found by Carpenter and Keeling. Both of these have been attacked with intention to explain or discredit them. Osmond has suggested in regard to the 800° inversion that the surfaces of the test specimens used in the cooling curve work had become decarbonized by heating in air, and thus gave a slight heat evolution corresponding to the β to α inversion in the low carbon specimens. We must remember that some supercooling occurred in the cooling curve work, and that supercooling would be especially effective on a weak inversion. The *characteristic* temperature of an inversion is the *highest* temperature found for it in cooling curve determination. The characteristic temperature of the "800° inversion" is at least 800°; the characteristic temperature of the β to α inversion is 785°. Therefore M. Osmond's suggestion cannot explain the 800° inversion.

It is most interesting here to show how M. Osmond was misled into his suggestion. During the freezing of a melt

[1] E. S. Shepherd: Jour. Phys. Chem., **8**, 421 (1904).
[2] Shepherd and Blough: Ibid., **10**, 630 (1906).
[3] B. E. Curry: Ibid., **11**, 425 (1907).

of say 1 percent carbon the first crystals coming out of the melt, as can be seen by inspection of the liquidus and solidus lines of the diagram, would contain only 0.5 percent of carbon. Consideration of the beautiful pictures taken by Goerens and Gutowski[1] shows that the melt in contact with these crystals remains of higher carbon content than the average, and finally solidifies to an adjacent crystal with considerably more than 1 percent of carbon. *Adjacent crystals in the iron-carbon alloys are not then of equal carbon content, but vary oppositely from the average carbon content, and the variation may be decidedly large in relation to the average carbon content.* Diffusion, which theoretically should go on, is slow even in the melt, and is still slower in the solid. So it comes about that because of the heterogeneity of carbon content of adjacent crystals, a 1 percent specimen is capable of giving inversions which really belong with carbon contents both above and below its average carbon content. It is through this phenomenon that the gap between the β to α inversion in the low carbons and the 800° inversion in the high carbons is bridged over in the cooling curve determinations. This same phenomenon explains also the experimental difficulty of locating by cooling curves the inversions along the sloping lines between the γ field and the fields of $\beta + \gamma$ and $\alpha + \gamma$. (Fig. 2).

Rosenhain has offered as explanation for the 600° inversion a change in the quartz used in construction of the furnace. As the characteristic temperature of this quartz inversion is 585°, while that of the "600° inversion" is 615°, this suggestion of Rosenhain's may be dismissed, for it is obvious that a change in furnace material at 585° could hardly cause and account for an apparent inversion in the cooling curve specimens at a temperature 30° higher.

As the cooling curves do not give data as to vertical or steeply sloping lines in the equilibrium diagram, we must

[1] Experimentelle Studie über den Erstarrungs- und Schmelzvorgang bei Roheisen, Metallurgie, **5**, 137 (1908).

seek elsewhere for evidence of such lines meeting the horizontal lines of these new inversions. One bit of evidence is found in the analysis of the specimens used by Carpenter and Keeling in the cooling curve work. A similar set of specimens is taken from some work by Wüst.[1] All of these specimens of both sets were practically pure iron-carbon alloys, and were furnace cooled. In Fig. 4 I have plotted the values of graphite against total carbon content. It is at once notice-

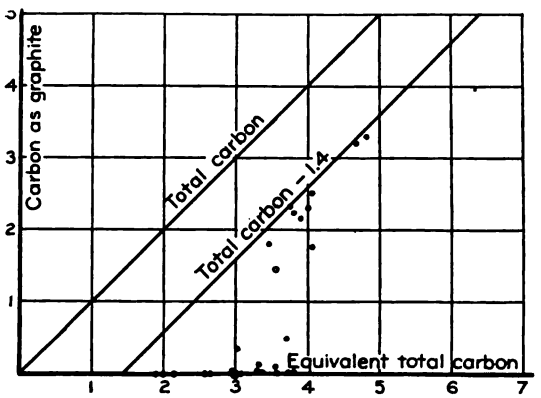

Fig. 4

able that up to 3.5 percent total carbon the graphite remains low, while above 3.5 total carbon the graphite approximates to total carbon minus 1.4 percent. Since the reaction between iron and graphite is very slow below 800°, this disposition of graphite with reference to total carbon must have originated above 800°. There is then in the equilibrium diagram above 800° some kind of a critical line, or field, at 3.5 percent carbon. (For detailed tables of numerical data see the paper on "The Iron-carbon Equilibrium," cited above).

The graphite to total carbon relation discussed above was a relation arising during slow *cooling* of the alloys. It is desirable to show that the same relation is reached by *heating*. Saniter[2] took artifically prepared Fe_3C and heated it in a

[1] Iron and Steel Mag., 11, 185 (1906).
[2] Metallographist, 5, 215 (1902).

nitrogen atmosphere to a temperature of 800° to 1000° and cooled slowly. His work may be tabulated as follows:

Material analyzed	First sample		Second sample	
	Combined C Percent	Graphite Percent	Combined C Percent	Graphite Percent
Original carbide.....	6.73	0.19	6.46	0.22
After heating in nitrogen to 800° and gradually cooling..	5.72	0.40	—	—
After heating in nitrogen to 1000° and gradually cooling..	*3.63*	2.50	*3.79*	2.41

His temperatures were only approximate. The significant analyses are italicized. *The conclusion is that cementite, on heating into the range 800° to 1000°, breaks down into graphite and some iron carbon phase in which the iron retains in combination or solution about 3.6 or 3.7 percent of carbon.*

Now it is interesting to note that the chemical compound Fe_6C would contain 3.46 percent carbon. Accepting this as at present the simplest supposition for that phase which has a critical concentration at 3.5 percent carbon, the fields of the equilibrium diagram above the 800° inversion become as in Fig. 2, $\gamma + Fe_6C$ and Fe_6C + graphite. Saniter's heating of Fe_3C was not long enough to reach a definite equilibrium even at the higher temperature, so there is no contradiction between the 3.6 or 3.7 from Saniter's work and the 3.5 percent from the relation of graphite to total carbon. The 800° inversion becomes the change from $\gamma + Fe_6C$ or Fe_6C + graphite to $\gamma + Fe_3C$. *Cementite is not stable above 800°.*

The question next to be answered is: Is cementite stable at any temperature? Troost and Hautefeuille, Campbell, and Moissan, have all reported that the reaction for formation of Fe_3C from its elements is endothermic. It is a familiar statement that endothermic compounds are unstable com-

pounds. Therefore cementite is unstable. This is the course of reasoning which is at base responsible for the whole of the hypothesis of a double system of stable and metastable equilibria. In the sense in which the words stable and unstable are used by the physical chemist in discussion of chemical equilibria, the question whether a compound is endo- or exothermic has nothing to do with the stability of the compound. The familiar statement to the contrary is false. We recognize two criteria of equilibrium, the phase rule and that general law known as the theorem of LeChatelier, stated as follows by Ostwald:[1] "If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint, that is, one by which its effect is partially destroyed." Now in the production of an endothermic compound from its elements we may add heat at constant temperature, and the formation of the compound absorbs heat at constant temperature. We try to add heat and raise the temperature, and the reaction opposes the rise of temperature. There is nothing in this contrary to the phase rule or the theorem of LeChatelier. The statement that endothermic compounds are unstable is a historical vestige from those days of chemistry before physical chemistry was invented, and according to the now well-known laws of physical chemistry the statement is incorrect and unjustified.

The criterion which must be met is that all inversions occurring in cooling of any composition in the alloy series must show evolution of heat, while in heating all inversions must show absorption of heat. Such is the case with all of the inversions shown by the diagram of Fig. 2. There is nothing in this diagram inconsistent with any of the laws of physical chemistry. The only question which can be raised is that of the identification of the various phases—whether something else might replace Fe_6C, or Fe_3C, or Fe_2C. *But these must stand until that something else is found.*

[1] "Principles of Inorganic Chemistry," p. 133 (Macmillan, 1904).

Fe_3C has been found too frequently, and identified too carefully, for any doubt to remain that such a compound exists and plays an important part in our iron-carbon alloys. I must then bring evidence that Fe_3C is formed within those fields of temperature and concentration in which I have placed it on the diagram. Margueritte[1] carbonized in an atmosphere of carbon monoxide finely divided metallic iron made from the oxalate, using temperatures of "low cherry red" and "bright cherry red." He obtained a combined carbon content of 6.60 percent and 6.55 percent respectively. Fe_3C requires 6.67 percent carbon. This work is remarkable in that it was done before Fe_3C was known as a compound. The temperatures correspond approximately to the lower and upper edges of the fields in which Fe_3C is placed in Fig. 2. Charpy[2] carbonized steel filings containing 0.09 percent carbon in an atmosphere of potassium cyanide at a temperature of 650°, heating in one case for 85 hours and in the other for 110 hours. In each case he obtained 6.72 percent of combined carbon, which is within the errors of analysis of the composition of cementite. 650° comes near the lower edge of the $\alpha + Fe_3C$ field in Fig. 2. Offerhaus and Howe[3] heated powder of pure electrolytic iron in potassium cyanide for various periods of time at 650°. Their results may be tabulated:

	Time from beginning		
	14 hours Percent	31¾ hours Percent	50 hours Percent
Combined carbon...	5.19	5.74	6.75
Graphite.....	0.11	2.38	2.88
Total carbon.....	5.30	8.12	9.63

If a curve be plotted from these results of combined carbon against time of heating, this curve will be found

[1] Comptes rendus, **49**, 726 (1864).
[2] Iron and Steel Mag., **8**, 305 (1904).
[3] Trans. Am. Inst. Mining Engineers, Feb., 1908.

asymptotic to the composition of cementite. This shows that the combined carbon was cementite from the beginning to the end of the process, and that at 650° any combined carbon in equilibrium in the iron-carbon alloys is Fe_3C.

The conclusion then holds that cementite is, within the limits given by the diagram in Fig. 2, a stable phase in the iron-carbon system. Saniter proved that it decomposes above 800°; Campbell and Kennedy[1] have shown that FeC_3 changes to Fe_2C below 600°. They annealed an iron (white charcoal iron) of 3.54 total carbon with only a few hundredths of 1 percent each of Mn, P, Si, and S, heating slowly to 950° and then cooling slowly. The recovered carbides were separated into fine grained and coarse grained portions by means of a 200-mesh sieve. The fine-grained carbide averaged 9.33 percent carbon and the coarse grained 7.74 percent. Fe_2C, if present, was a product of the decomposition of Fe_3C during the slow cooling. As such a decomposition product the Fe_2C should be finer grained than Fe_3C. The cooling was too rapid to give a complete inversion of Fe_3C to Fe_2C. The results indicate clearly that below 600° Fe_3C breaks down to Fe_2C. Fe_2C would have 9.67 percent carbon, which, considering the method of separation of the carbides, is checked with sufficient accuracy by the 9.33 percent found in the finer grained carbide.

Strohmeyer[2] has shown that there goes on in steels at ordinary temperatures, and more rapidly as the temperature is raised, an inversion which increases the brittleness of the steels. The phenomenon known as "Stead's brittleness" must be this same change. The embrittling of steel by working at a "blue heat" comes back to the same inversion for a cause. All of these phenomena require for their explanation some change in the steels at a temperature below 700°; all are satisfied by the Fe_3C to $\alpha + Fe_2C$ change as the explanation of the inversion found by Carpenter and Keeling at 615°.

[1] Jour. Iron and Steel Inst., 1902, ii, 288.
[2] Ibid., 1907, i, 200.

In the data to be considered from this point on we have to deal not with pure iron-carbon alloys, but generally with commercial forms in which besides iron and carbon there are present sulphur, phosphorus, silicon, and manganese. It is necessary to establish the effect of addition of each of these elements on the iron-carbon relations in the alloy. Max Orthey has published[1] data showing that the addition of these elements, one at a time in varying amounts, affects the graphite content of cast irons when the cooling rate and the contents in all other chemical elements are held constant. To a cast iron of 3.5 percent total carbon he added the other elements, with the results shown in Figs. 5, 6, and 7. Remembering that the graphite content of the cast irons has its origin at or above 800°, these figures show the effects of silicon, phosphorus and manganese on the relations of iron to carbon at temperatures above 800°. An addition of 1 percent of silicon increases graphite, or decreases solution carbon, by 0.45 percent; phosphorus acts in the same direction, but to a much less extent; manganese acts in the opposite direction to a slight extent. In the article on "The Iron-Carbon Equilibrium" I gave the probable interpretation of these effects of the addition of other elements as follows: Silicon displaces carbon, atom for atom, in the solid solution of carbon in γ iron. The displaced carbon appears as graphite. Carbon displaces phosphorus from solution in the iron, and the phosphorus then goes into the form of Fe_3P. But the phosphorus in Fe_3P uses up some of the iron which might otherwise be caring for carbon; and so there results an increased concentration of carbon in that part of the iron which remains uncombined with phosphorus. Sulphur acts like phosphorus, but as FeS does not use up iron as fast in relation to sulphur as Fe_3P does in relation to phosphorus, the effect of sulphur on the carbon is much less relatively than that of phosphorus. Manganese acts in the alloy like a

[1] Metallurgie, **7**, 199 (1907). For full data see the original, or tables in the article "The Iron-Carbon Equilibrium," cited above.

more active variety of iron; as manganese can take care of more carbon in solution than iron can, addition of small amounts of manganese increases the solution carbon and decreases the graphite.

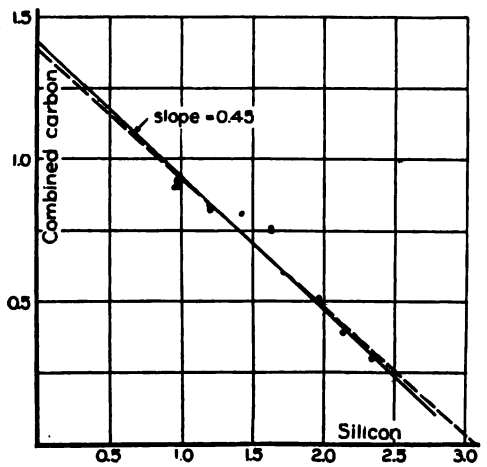

Fig. 5

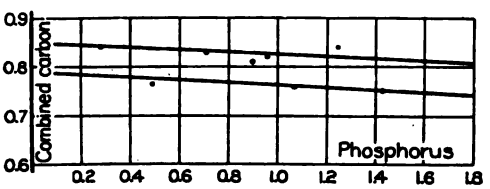

Fig. 6

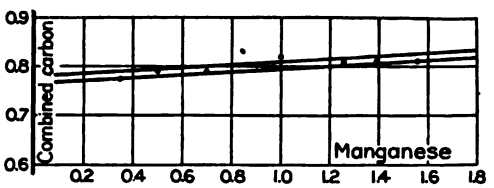

Fig. 7

I have shown above (Fig. 4 and discussion) that in pure iron-carbon alloys of more than 3.5 percent carbon, graphite approximates to total carbon minus 1.4 percent. In these alloys an addition of 1 percent of carbon would mean an in-

crease of 1 percent in graphite. Now calculating the effects of the other elements according to the preceding paragraph, addition of 1 percent of silicon would increase graphite by 0.45 percent, if all other quantities remained unchanged. Similarly, addition of 1 percent phosphorus would increase graphite by 0.12–0.15 percent, and 1 percent sulphur would cause 0.05 percent more graphite. One percent manganese would decrease graphite by 0.03 percent. Now these various effects could be secured in the pure iron-carbon alloys by changing the total carbon by +0.45 percent, +0.12 percent, +0.05 percent, and —0.03 percent respectively. Therefore in studying the commercial iron-carbon alloys and the relation of iron to carbon for graphite formation in such alloys we may replace the elements manganese, silicon, phosphorus, and sulphur by equivalent amounts of carbon, calculating the equivalents by means of the displacing ratios above. A pure iron-carbon alloy with a carbon content equal to the summation from the commercial alloy of (total carbon + 0.45 × silicon + 0.12 × phosphorus + 0.05 × sulphur — 0.03 × manganese) would have the same graphite content as the commercial alloy. The silicon of the commercial alloy would be in solution in iron; the phosphorus and sulphur would be present as Fe_3P and FeS or corresponding manganese compounds; the manganese would be acting, if combined with carbon or silicon, like a more active iron. If the manganese forms Mn_3 P or MnS we still have, on account of the difference of atomic weights of manganese and iron, a given weight percentage of manganese in the alloy more effective than the same weight percentage of iron in the ratio 55.9/54.9 or 2 percent better. Therefore so far as displacing power of manganese is concerned it makes no appreciable difference what the manganese does in the alloy; all of its possible actions lead to the same value of displacing power. It is understood that this use of an "equivalent total carbon" for the commercial alloy refers to conditions arising above 800°.

Being now able to make numerical allowance for the

extra elements present in commercial irons, we can take up and consider, in relation to the equilibrium diagram, a very large collection of data from which we were hitherto barred. I desire first to call attention to Fig. 1, and the solubility line there given for carbon in γ iron in the "stable" system between 800° and the liquid eutectic. The iron which Benedicks used for the determination of the line contained C 3.9 percent, Si 0.75 percent, Mn 0.37 percent, S and P negligible. Applying our displacing powers for a correction due to Si and Mn, we find that there was in solution in the iron the equivalent of 0.33 percent carbon for which Benedicks gave the iron no credit. If this 0.33 percent be added to the carbon shown on the diagram as stable in solution, the full line is moved over to the dotted line, and we have the startling and interesting result that in this case of experimental determination of lines of the "stable" and "metastable" systems, the lines of the two systems are coincident throughout within the error of experiment.

The believers in the "metastable" system iron-iron carbide say that this system is realized by rapid cooling of the melt. Any reheating of the metastable solid, increasing the molecular freedom, then means a change toward the stable system; and continued heating and cooling of the solid should result finally in doing away with all of the metastable phases, and leave only the stable ones. It is obvious from physico-chemical reasons that once having thus brought the solid into the stable condition it could not be made to show or develop again any of the metastable phases without being taken through a process of melting and rapid cooling from the melt. Yet when Benedicks heated and cooled repeatedly the iron mentioned above, the cementite inversion at 700° became stronger, not weaker, with each repetition. And when after the iron had been "reduced to the stable condition of ferrite and graphite," the iron was heated up to 940° and cooled, the structures martensite, pearlite, cementite, etc., characteristic of the "metastable" system, were found. Which is to say that Benedicks' own

experiments for determination of the limits of the stable and metastable systems furnish the best of proof that no such thing as the supposed metastable system exists, and that cementite is a part of the real stable equilibrium diagram for iron and carbon.

To check whether the commercial cast irons would fall into line and give such a relation of graphite to total carbon as was found in the pure iron-carbons (Fig. 4), I collected a large number of complete analyses from various reliable sources, calculated the "equivalent total carbon" for each analysis, and then plotted Fig. 8. The sources for the analyses used were such standard books as Ledebur's Eisenhüttenkunde. A full table of the numerical data will be found in the article on "The Iron-Carbon Equilibrium" in the Journal of Physical

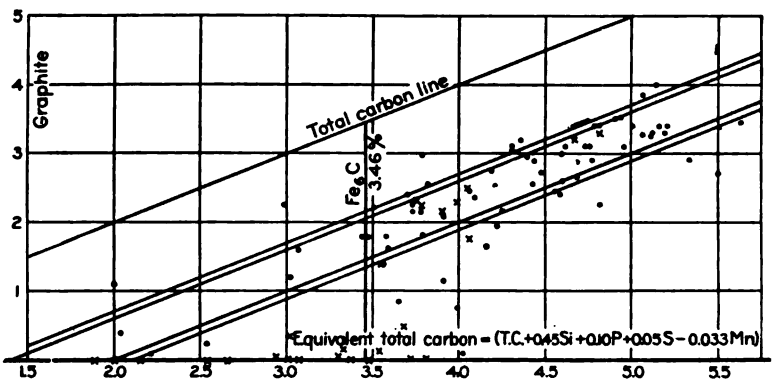

Fig. 8

Chemistry for October, 1908. Fig. 4 is repeated in Fig. 8 by the × points. The data in Fig. 8 represent commercial cast irons. It is evident at once that the commercial cast irons do act in the same way as do the pure iron-carbon alloys. All of the three points which fall above the line (total carbon minus 1.3 percent) in Fig. 8 are from analyses of *mottled* irons (irons in which the carbon distribution is not uniform). Referring to Fig. 2, it is evident that with fairly rapid cooling of the casting we might expect to realize a graphite content corresponding to point B, or graphite equal to (equivalent

total carbon—2.1 percent); while with slow cooling we should get also the breakdown of γ solid solution along the line BC, and should realize a graphite content equal to (equivalent total carbon—1.3 percent). The two double slanting lines in Fig. 8 correspond to these two limiting values of graphite; the figure shows how well the actual graphite falls within these limits. By holding the iron long enough at 1100° the graphite corresponding to C, Fig. 2, can be realized in any iron. Hence the points in Fig. 8 between the lines (equivalent carbon—1.3 percent) and (equivalent carbon—2.1 percent) and with equivalent carbons less than 3.5 percent represent not impossibilities, but abnormalities.

This use of the "displacing powers," and the calculation of "equivalent total carbon" has an exceedingly important practical application. For by this calculation it becomes possible to tell from the total carbon, silicon, manganese, phosphorus, and sulphur just what the graphite content of a gray cast iron may be expected to be. Only one other important variable is left, the cooling rate during freezing. This is usually entrant in the problem through the size and shape of the castings. With the effect of cooling rate known the distribution of the total carbon in the solution and graphitic forms is determinate, and therefore the physical properties of the metal. On account of the low values of displacing powers for sulphur and manganese, these elements may usually be neglected in computing the equivalent total carbon. This useful quantity is given with sufficient accuracy by (total carbon + 0.45 × silicon + 0.12 × phosphorus). I should mention that nitrogen, which is not usually determined in analyses, though generally present, has the decidedly high displacing power of about 0.2. (Nitrogen actions are similar to those of phosphorus).

Now we find everywhere repeated the statement that phosphorus, sulphur, and manganese tend to whiten cast irons. This certainly does not agree with the statements above as to displacing powers, that 1 percent of phosphorus increased graphite by 0.12 percent, and 1 percent of sulphur

increased it by 0.05 percent. But the derivation of the displacing powers was qualified by the premise "other things remaining the same." The displacing powers relate to actions of the carbon disposition in the solid metal. Phosphorus and sulphur have actions on the liquid metal which overbalance their effects in the solid—other things do not remain in general the same when phosphorus and sulphur are added.

In blast furnace or cupola melting, where the iron is in intimate contact with a carbonaceous fuel, the tendency of the cast irons is to run the total carbon content up toward a "saturation" value, which is really the carbon content of the liquid eutectic. When silicon is added to a melt of iron and carbon the liquid eutectic carries less carbon than does the eutectic of iron and carbon alone. A similar fact is true of phosphorus and of sulphur. Manganese increases slightly the carbon content of the eutectic. Now with silicon this effect on the melt of the cast irons is overbalanced by the displacing power of silicon on carbon in the solid metal—the net effect of silicon addition is an increase of graphite. With sulphur and phosphorus the reduction in total carbon by the action of the elements in the melt is preponderant over the displacing powers in the solid; the net effect is an iron with less graphite. This is true, however, only because the total carbon content of the high phosphorus or high sulphur iron has been so lowered as to mask the real effect of the sulphur or phosphorus in the solid metal.

Wüst and Peterson have determined the numerical value of the reduction of carbon content of the liquid eutectic by the addition of silicon.[1] Their analyses plot upon a very good straight line of the equation C percent $= 4.23 - 0.269 \times$ percent Si. (Fig. 9). One percent of silicon added then means, in cupola or blast furnace melting, a reduction of 0.269 percent in the total carbon. But since the action of this 1 percent of silicon in the solid metal is to increase graphite

[1] Metallurgie, 3, 811 (1906).

by 0.45 percent, we will have by the addition of the silicon a net gain of 0.18 percent graphite for each percent of silicon.

It is a peculiarity of this addition of silicon which I believe has not hitherto been explained that after the silicon reaches 3.0 percent further addition of silicon does not increase, but on the contrary decreases, the graphite content. I have already shown that the amount of carbon normally remaining in solution in the pure iron-carbon cast iron is 1.3 + percent. The amount necessary to displace all of this solution carbon is (1.3 +) ÷ 0.45, or 3.0 percent. That is to say, if 3 percent of silicon is added to a medium to high carbon content, then *all* of the carbon will be graphite. Now if still more silicon is added, the only effect which can be felt is that upon the melt, reducing the total carbon, and since all carbon is now graphite, reducing the graphite also.

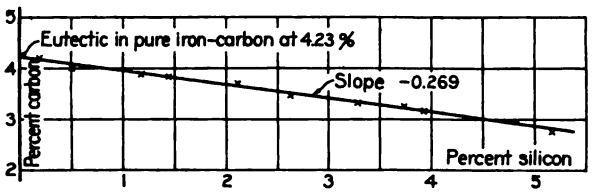

Fig. 9

The effect of phosphorus on the liquid eutectic is similar to that of silicon, reducing the carbon content. The numerical value of the effect is —0.32.[1] For sulphur the only determination I have found is an old one by Weston, quoted in Ledebur's Eisenhüttenkunde, p. 307–8. The numerical value is —0.3. The value of —0.27 for silicon and —0.32 for phosphorus are good up to additions of about 10 percent and 7 percent respectively of silicon and phosphorus. The value —0.3 for sulphur has been checked up to a little over 2 percent of sulphur. These limits are all far beyond the amounts of silicon, phosphorus, and sulphur ever present in commercial cast irons.

Comparing the effects of phosphorus and sulphur in the

[1] Wüst: Metallurgie, 5, 86 (1908).

liquid with their effects in the solid, we find the net result of an addition of 1 percent of phosphorus to an iron *which can take its carbon to saturation in the liquid state* is to increase graphite by —0.32 percent +0.12 percent, or a numerical *decrease* of graphite content of 0.20 percent; for 1 percent sulphur the net result is —0.3 percent +0.05 percent, or a graphite decrease of 0.25 percent.

I have now analyzed the ways in which silicon, phosphorus, sulphur, and manganese affect the total carbon content of "saturated" cast irons, the distribution of the total carbon in the forms of solution carbon and graphite, and the net values due to combination of both, and have shown the numerical values of the different effects for each element. The expectation of total carbon in a saturated cast iron is (4.25 —0.27 × silicon — 0.32 × phosphorus —0.3 × sulphur + 0.03 × manganese). The "equivalent total carbon" is (total carbon + 0.45 × silicon + 0.12 × phosphorus + 0.05 × sulphur — 0.03 × manganese). The graphite expectation is "equivalent total carbon" minus a constant, which constant depends on the cooling rate. With the slowest cooling the constant has the value 1.35. With quicker cooling the constant is larger. Its average value is 1.7; it does not go over 2.1 unless the cooling is so rapid as to be properly called chilling. In the presence of very high silicon (over 3 percent) one must remember that the graphite cannot exceed the total carbon present. Silicon goes into solution in γ iron, displacing carbon from such solution. The equivalence in effects of 1 percent of silicon and 0.45 percent of carbon (atomic displacement) seems to hold whether the content in either or both elements be low or high.

It is very easy now to make out rules for getting most readily certain kinds of cast irons. Carbon in solution makes a hard and brittle metallic part in a cast iron; silicon in solution a relatively soft and tough metallic part. Phosphorus and sulphur go with low total carbon, but high "combined" carbon. ("Combined" carbon is really solution carbon in the cast irons). Phosphorus brings a decided depression of

the temperature of the liquid eutectic—makes an iron fluid to lower temperatures. The eutectic with iron-carbon-silicon is slightly higher in temperature than that of the pure iron-carbon. Manganese helps as in steels to freedom from FeS and FeO, and so gives sounder material. Shrinkage is controlled by the graphite content.

The metallographic nature of the cast irons

As a preliminary to the consideration of the metallography of the cast irons, it is necessary to discuss the varying effect of cooling rate upon iron carbon alloys as carbon increases. In commercial working it is impossible to harden steels with less than 0.3 percent carbon. Such hardening, which really means cooling at such a rate as to suppress and prevent the inversion of the γ solid solution to forms normal at lower temperatures, is quite possible in laboratory working even with carbon as low as 0.1 percent. With increase of carbon the hardening is more and more easily carried out —the cooling rate which will suppress the γ inversion is less the higher the carbon content. When the carbon content reaches that of the cast irons the cooling rate which is found in the making of castings in sand molds is great enough to suppress practically all of the γ inversion. That is, the cast irons as cast consist metallographically of two parts: carbon as graphite, mixed with a metallic matrix which is a solution of carbon and silicon in γ iron. The physical and engineering properties of the material are those of the matrix modified by the admixture of the graphite. The effect of the graphite is much larger than would be expected from its weight percentage, first because the graphite is much less dense than the iron and secondly because the graphite, if formed by crystallization in contact with liquid alloy, is disposed in thin plates. The density of graphite is 2.25, of the matrix about 7.6; hence a certain weight percent of graphite brings a volume percentage 3.3 times as great. The fact of plate crystallization of graphite increases again the weakening due to the volume content of the graphite. The

hardness, strength, etc., of the metallic matrix depend on the content of carbon and silicon in solution. Phosphides and sulphides of manganese or iron are of course mixed in with the metallic matrix. As the matrix itself is more or less brittle, these phosphides and sulphides are not relatively so important in the cast irons as in the steels. High carbon in solution in the matrix makes a brittle, hard, and unworkable iron; high silicon in solution makes a softer, tougher, and more workable material.

Gutowsky has recently studied the freezing of a high phosphorus cast iron.[1] By quenching in ice water a very small specimen of the iron he obtained for microscopic examination the structure which the iron had taken at various temperatures. His work shows that there is no change in the structure below 950°—that is, all inversions below 950° are suppressed. 950° was the freezing point for this iron, due to the presence of the phosphide eutectic. Practically then the structure of the cast irons as cast is that which originates during the freezing. Although some of the stronger inversions below the freezing point, notably that at 725°, can be found in the cast irons, the effect of these inversions on the structure as a whole is insignificant. It must be remembered that the matrix of the cast irons is not a homogeneous structure, but instead is a conglomerate of γ solution crystals with varying contents of silicon and carbon in solution. The crystals which form first during the freezing are much lower in carbon and silicon than those which form later. It is probably a few of the lowest carbon crystals only which invert at temperatures below the freezing point.

The above paragraphs have outlined the nature of the gray cast irons. The white cast irons are more of a problem. Knowing now that cementite is unstable and does not originate in the iron-carbon equilibrium at temperatures above 800°, the "metastable equilibrium" hypothesis that white cast irons represent the system iron-iron carbide is untenable.

[1] Metallurgie, 5, 463 (1908).

White cast irons are formed by very rapid cooling of the melt. By preference a melt is used of such composition that there will not be a large tendency to form graphite during the freezing. However, with rapid enough chilling any iron can be cast white and graphiteless. I have already indicated that, in the case of gray cast iron, the iron goes through the transformation indicated at the liquidus and solidus lines of the equilibrium diagram, and that below the freezing point all other inversions are suppressed. By extension of the argument, the chilling of the white cast irons suppresses also the graphite formation during freezing. There are two possible explanations of the metallographic nature of the white cast irons. The first is that, as with the making of amorphous selenium from the melt, the solid formed is really a supercooled liquid. The second explanation is that by the rapid cooling we realize an extension to low temperatures of the lines AD and AB (liquidus and solidus) of Fig. 2. There are always present in white cast irons some crystals obviously of that type of γ solution crystal which separates from the melt. I prefer the second explanation, and state the nature of the white cast irons to be a supersaturated solution of carbon (and some silicon) in γ iron. As with the metallic part of the gray cast irons, individual crystals of this supersaturated solution are of different carbon contents. Hence the apparent "cementite plus pearlite" structure of the white cast irons. The "cementite" patches or crystals are those crystals of γ solid solution which first froze out of the melt; the "pearlite" is the mass of the melt, caught and held as a supersaturated solid solution. The physical properties of hardness, strength, etc., of the white cast irons are the same as those of the matrix material of the gray cast irons, if proper allowance be made for the difference in amounts of carbon and silicon in solution in the γ iron.

If the white cast iron be reheated, it is to be expected that the first reaction to occur will be the one which was suppressed during the chill casting, *viz.*, the formation of graphite. This means the reduction of the supersaturated

solid solution back to saturation. The saturation line for graphite in contact with carbon solution in γ iron is the line BCY of Fig. 2. The white cast iron, on reheating to a red heat, will then form graphite internally until the *equivalent* carbon in solution reaches the value shown by BCY. Since this line shows decreasing carbon in solution with reduction of temperature, more graphite will be formed the lower the temperature at which the white cast iron is annealed. That such is the case has many times been shown. This graphite formed in the solid is very finely divided, almost microscopic and uniformly distributed in the iron. It is called, from the treatment which leads to its formation, temper carbon or temper graphite. Because of its fine division and uniform distribution, temper graphite is much less detrimental to the properties of the metal than is the graphite which has crystallized out in plate crystals in contact with a liquid melt. Usually it is difficult to start the formation of temper graphite below 800°. The presence of silicon or of a little graphite from the freezing acts as a starter for the reaction. After the formation of temper graphite is once started, it will continue at quite low temperatures.

Sometimes even a suspended equilibrium may be obtained along CY which is nearly a production to lower temperatures of the line CLN, Fig. 2. Such a suspended equilibrium is occasionally found in high carbon steels which have been annealed for a long time at high temperature and very slowly cooled. This suspended equilibrium will be ended by the occurrence of the inversion which normally comes at 725°. A steel is not likely to start the production of temper carbon unless it has at some time in the annealing process been carried into the field γ + graphite in Fig. 2. The equivalent carbon must be as great as or greater than 1.35 for this to be possible. Having started the γ + graphite arrangement, it may continue along CY to quite low temperatures. If the high carbon steel came down normally to low temperatures, its structure would be pearlite + excess of cementite. If, however, a case of the suspended equilib-

rium mentioned above occurs in the steel, the structure comes out pearlite + temper graphite + ferrite. The thought would not be unnatural that the cementite had decomposed with formation of graphite. Cementite disappears in the heating of high carbon steels, at about 900° (for then γ + cementite becomes $\gamma + Fe_6C$, by Fig. 2); if the heating is carried no further the cementite will reappear on cooling. If the heating is carried to the γ + graphite field, then the steel may cool along the course of the suspended equilibrium, *which is the line showing the solubility of graphite in γ iron.*

Malleable cast iron is made from white cast iron by annealing at red heat. Temper graphite is produced in the annealing as explained above. The structure of the iron is then reduced to temper graphite + solid solution of carbon and silicon in γ iron. The equivalent carbon content of the solid solution should be at this stage about 1 percent. Usually the castings are annealed in an oxidizing atmosphere or packing. By this, both temper graphite and solution carbon are oxidized out of the surface layers of the castings. Then follows migration of solution carbon outwards from the center, to replace the loss in the outer surfaces. This migration of solution carbon may be accompanied by a counter migration of silicon. When the iron is cooled after the annealing, the γ solid solution becomes $\alpha + Fe_3C$, or since usually little solution carbon is left, α ferrite plus a small amount of pearlite. The temper carbon remains in the iron where it was formed, except at the surface where it was oxidized.

To show that the malleable cast irons produce temper graphite to the same proportions as ordinary gray irons do flake graphite, I have plotted in Fig. 10 graphite against equivalent total carbon from a series worked out by Charpy and Grenet.[1] Comparison of this diagram with Fig. 8 will show the identity of the two cases. The reheating of the

[1] Metallographist, 5, 202 (1902); Bull. de la Soç. d'Encouragement, March, 1902.

white cast iron simply enables it to develop graphite as it normally would have done during freezing, if the cooling had been slow. If one starts with the assumption that the white cast iron is made of cementite, then necessarily we have here cementite decomposing at a temperature (700–800°) where continued heating is known to produce, not decompose, the cementite. But calling the white cast iron a supersaturated solution of carbon and silicon in γ iron, the graphite production on annealing is entirely normal and what one would expect. It is a first step toward the equilibrium relations.

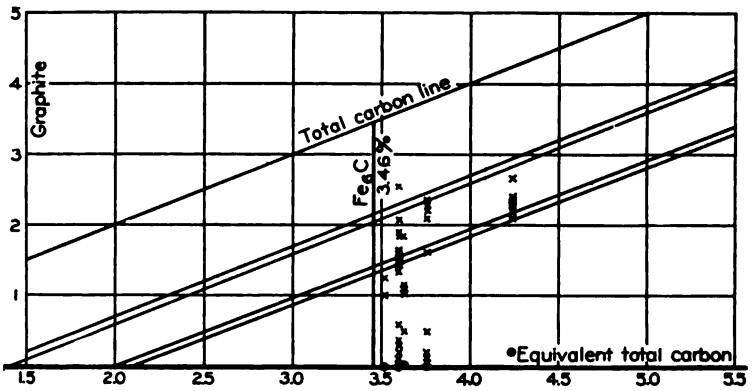

Fig. 10

I can now assemble the metallographic formulas for the structures of the cast irons. Gray cast iron has crystalline flake graphite mechanically mixed with a metallic matrix which is a solution of silicon and carbon in γ iron. White cast iron is a supersaturated solution of carbon and silicon in γ iron. Malleable cast iron has temper graphite mechanically mixed with a metallic matrix which is α iron, ferrite, with more or less pearlite. In case the suspended equilibrium persists, malleable cast iron has temper graphite mechanically mixed with a solid solution of carbon and silicon (each in slight amount only) in γ iron. I do not believe this case occurs, but it is possible. The "formulas" just given neglect phosphides and sulphides of iron or manganese, which can be understood as being mechanically mixed, as eutectics, with

the metallic matrices. None of the irons as cast are homogeneous from crystal to crystal, because of the selectiveness of the freezing of the alloy and of the slowness of diffusion.

In view of the outline above of the nature of the cast irons, and of some peculiarities of high carbon steels, the question becomes pertinent: where does the equilibrium diagram, as shown in Fig. 2, come in in commercial iron-carbon alloys? The truthful answer must be that when equivalent carbon passes 2 percent we no longer have to do in commercial alloys with equilibrium relations. Up to a carbon content of 1.3 percent the diagram of Fig. 2 is realized in commercial working. Commercial heat treatments are too short to bring any of the irons of the higher carbon contents to equilibrium. A steel of 1.8 percent carbon when heated to 900° has its cementite disappear and goes over into the structure $\gamma + Fe_6C$, which is decidedly different in appearance. This has been shown by Arnold[1] though of course Arnold did not name the new structure as I have. But a 1.8 carbon steel is not a commercial steel. The structure called by Osmond "martensite plus austenite" is really the structure of the field $\gamma + Fe_3C$ in Fig. 2. This structure may be found occasionally in some special high carbon steels. The heat of reaction for the formation of Fe_6C is very small, and the production of Fe_6C exceedingly slow. Hence we do not have it occurring in appreciable amount in any commercial product. Something of the same nature holds true of Fe_2C. Fe_2C is slowly formed in "soft" steels—that is, those which have supposedly ended their heat treatment in the $\alpha + Fe_3C$ condition. But where we might from the equilibrium diagram expect most of Fe_2C, in the cast irons, it does not usually occur at all. It cannot very well occur there because Fe_2C comes from the decomposition with lowering temperature of Fe_3C, and without heat treatment after casting the cast irons do not contain even appreciable amounts of

[1] "Thermal Transformations of Carbon Steels," Iron and Steel Inst. Jour., 1905, ii, p. 39 et seq.

Fe_3C. Where the equilibrium diagram of Fig. 2 comes into use is in giving a consistent basis of reasoning as to the direction in which changes should go. If, say, a white cast iron is heated in a vacuum at 1000°, it should first form temper graphite and by that reduce the carbon in solution to the saturation amount; then, and then only, should the formation of Fe_6C begin to take place and graphite to disappear again. Commercial heat treatments stop short of the time necessary for the real equilibrium.

It is one of my aims in this paper to show that the theory of a metastable equilibrium of the system iron-iron carbide, mixed with a stable equilibrium of the system iron-graphite, is unnecessary for the explanation of the phenomena of the steels and cast irons. Convenient to this purpose is a paper by Professor H. M. Howe on the "Carbon-iron Diagram" in the Transactions of the American Institute of Mining Engineers for 1908. This paper gives a résumé of arguments for the double equilibrium system and for the Roozeboom diagram. I shall show how with the new diagram, Fig. 2, the objections to the Roozeboom type of equilibrium disappear.

The Roozeboom diagram had cementite normal up to the line CG, Fig. 2. At CG the theoretical reaction was formation of cementite from γ iron and graphite. *This reaction is endothermic while the cooling curves show an exothermic reaction at CG.* The objection disappears with the new diagram because the reaction of formation of Fe_3C from its elements does not appear in the new diagram.

Cementation and malleablizing do not obey Roozeboom's theory. I have explained them above in harmony with the new diagram.

The change of combined carbon (Fe_3C) into iron + graphite takes place at all temperatures between the freezing point and 650°. This is only partially true. By the new diagram cementite is unstable and disappears above 800°. The decomposition of cementite, so-called, in the white cast irons does not occur because what is called cementite in the white

cast irons is not cementite, but a supersaturated solution of carbon in γ iron for which the decomposition in annealing is entirely normal. I have also explained the apparent decomposition of cementite in the annealing of high carbon steels. This is quite a different phenomenon from that in the cast irons. All of the arguments for the double diagram based on the graphitization of cast irons fall down with the new explanation, given above, of the metallographic nature of the cast irons.

Rapid cooling yields cementite and slow cooling yields graphite. Rapid cooling yields a supersaturated solution of carbon and silicon in γ iron, not cementite.

Eutectic cementite very soon after its formation begins changing into graphite. The so-called eutectic cementite is not cementite, but γ solution. Its decomposition after freezing is shown by the line BC, Fig. 2.

Goerens and Gutowsky[1] *state that the graphite which forms in and near the freezing range comes from the decomposition of the eutectic cementite.* As Professor Howe remarks, there is no proof of this statement either in the work of Goerens and Gutowsky or elsewhere. As a matter of fact, all of the cementite visible in the photomicrographs of Goerens and Gutowsky is present obviously as a decomposition product of austenite (γ solution).

Bell, Brüstlein, Royston, Forquignon, Wüst and Schlosser, Arnold, Charpy, Charpy and Grenet, Tiemann, William Campbell, Arnold and MacWilliam, and Sauveur have reported cases either (1) of graphitization of white cast iron or (2) of graphite production in annealing of high carbon steels. These phenomena I have already discussed and explained in harmony with Fig. 2.

Saniter and Mylius, Förster, and Schöne report cases of change of isolated cementite to graphite production *at or above 800°*. I have already dealt in detail with Saniter's work. The results agree with Fig. 2.

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[1] Metallurgie, 5, 146 (1908).

Osmond repeatedly reheated and cooled a steel which had formed graphite by the suspended equilibrium method explained above. *The graphite recombined and the steel became again in structure a normal high carbon steel.* This shows that the graphitization of such steels is a result of some abnormal change, and that the cementite is really part of the stable equilibrium structure.

Heyn and Bauer reheated slowly cooled cast iron and found that the "combined carbon" increased. This agrees with a change toward the equilibrium of Fig. 2, in which finally no graphite is present until equivalent carbon passes 3.5 percent, at the temperatures 800° to 1100°. It does not agree with the double equilibrium hypothesis.

Royston got the same kind of results, starting with malleable cast iron—graphite recombines on heating.

The data of Mannesmann and others on cementation agree with CLN, Fig. 2, as giving the limiting carbon content of the γ solid solution. The results of Charpy and Grenet, working back from the cast irons, agree substantially with the line CY of Fig. 2 as giving the curve of solubility of graphite in γ iron. I have shown that this line also explains the graphitization of high carbon steels during annealing.

I have now set side by side the two hypotheses—that of the double equilibrium and that of the modified Roozeboom diagram. I have tried to show that the latter alone is competent to account for and explain the phenomena not only of the low carbon steels, but also of the high carbon steels and of the cast irons. In the introduction of the displacing powers I have tried to simplify the problems of the carbon distribution in the cast irons. I have outlined what I believe to be the real metallographic nature of the various kinds of the cast irons.

Cornell Universuty,
March, 1909.

NEW BOOKS

Photographische Probleme. *By Lüppo-Cramer. (Encyklopädie der Photographie. Heft 58.) 14 × 22 cm; pp. vi + 220. Halle: Wilhelm Knapp, 1907. Price: paper, 7.50 marks.*—This volume is based on the papers published by the author during the years 1902-1907. The subject is discussed under the headings: ripening of the emulsion; photochemical changes; the so-called chemical fog; the phenomenon of solarization; the photohalides of Carey Lea.

Under the ripening of the emulsion the chief points of interest to the author are the effect of the size of the grain and the so-called theories in regard to sensitizers. Under the heading of photochemical changes we find a discussion of the nature and reactions of the latent image. By chemical fog the author means the state of a silver bromide emulsion which can be developed without exposure to light. The author tries to prove that this state is different from that of a normal plate which has been fogged by exposure to light. In the article on solarization the author's aim is to show that all the theories of solarization are worthless and that Abney's is nearly the worst of them all. In the section on photohalides the author explains his belief that these substances are "adsorption compounds of silver halide and silver" and that they are identical with the substance forming the latent image.

This last is the one bit of constructive work in the book. While the volume is an exceedingly interesting one, it must be a bit discouraging to most people. It may be that the author knows too much about the subject or it may be a temperamental matter; but the fact remains that the author's attitude is represented by one of du Bois-Reymond's catch-words: "*Ignoramus.*" To the reviewer things do not seem so bad. It seems to him that many of Lüppo-Cramer's experiments can be explained in a way quite different from that adopted in the text. If that is done consistently, the photographic problems become quite simple ones—at any rate to one, like the reviewer, who is certainly not handicapped by an extensive practical knowledge of the subject.

Wilder D. Bancroft

The Theory of Valency. *By J. Newton Friend. Edited by William Ramsay. 12 × 19 cm; pp. ix + 180. New York: Longmans, Green & Co., 1909. Price:* $1.60.—The author devotes one chapter to the early theories of chemical combinations and another to the early theory of valency. Then we have two chapters on valency and the periodic law, followed by a series of chapters on the valency of the different elements. One chapter is devoted to Werner's theory, another to electrochemical theories, and the last one to a discussion of the physical cause and nature of valency.

The author accounts for such formulas as Cu_2Cl_2, Hg_2Cl_2 and others by considering the chlorine as trivalent. It is claimed that nickel acts only as a divalent metal, p. 117; on the other hand cobalt and iron are permitted to be both divalent and trivalent, p. 33. In view of the existence of hydrated nickelic oxide in the Edison cell, this seems to be an arbitrary and therefore an unwise distinction. The fact, that ammonium amalgam will precipitate metallic copper from a solution of a copper salt would seem to be pretty strong evidence

that there was something in the mercury besides ammonia and hydrogen, p. 83. On the other hand the author is willing to believe in the existence of the imaginary substances, CuAl and Cu_2Al, p. 155.

In the chapter on the physical cause and nature of valency, the following paragraphs, p. 167, seem worth quoting:

"It is well known that the numerical values of the valencies of those elements which exhibit variable valency usually differ by two, or multiples of two units. Thus gold is mono- and tri-valent. Nitrogen and phosphorus are tri- and penta-valent. Sulphur is di-, tetra-, and hexa-valent. So long as the old ideas prevailed, that the atoms were provided with hooks and eyes, which represented their valencies, a physical interpretation of the above was clear. But the demolition of these crude notions has rendered the explanation of multivalency more difficult.

"The suggestion of Barlow and Pope is, to say the least, very ingenious. Imagine an assemblage of close-packed spheres, and let one of these spheres have a valency volume m. If this is removed, and into the cavity thus produced a sphere of volume $m + 1$ is pushed, it will be clear that a second sphere, of valency volume 1, must simultaneously be introduced into the enveloping shell of atoms, if the close-packing is to be restored without remarshalling. This is obviously equivalent to the insertion of an atom of valency 1 in the space already occupied by an atom of valency m, and the filling of the gap thus produced in the enveloping shell by the insertion of a second atom of valency. 1. The atom of valency m will thus function as an atom of valency $m + 2$. Similarly, by pushing two atoms of valency 1, or what comes to the same thing, an atom of valency 2, into the space already filled by an atom of valency m either two atoms of valency 1, or one of valency 2, must be inserted into the enveloping shell. Consequently the atom originally exhibiting a valency m, now functions as an atom of valency $m + 4$. Sulphur is a case in point.

"It has already been pointed out, however, that all atoms exhibiting the same valency have not exactly the same valency volumes. For example, as any vertical column in the Periodic Classification is descended, a slight change in volume is exhibited, although it is not sufficient to change the valency by a whole unit. If, therefore, atoms of valency-volume exactly equal to unity are combined with other atoms of valency-volume intermediate between two whole members, it is clear that various assemblages may be formed, in which the numbers of monovalent atoms attached to one of the polyvalent atoms will not always differ by two. Molybdenum is a good example of this, for the di-, tri-, tetra-, and penta-chlorides, $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$, respectively, are known."

The author had a good subject and he has written a useful book; but that is all that he has done. The book is merely one of the series and nothing more.

Wilder D. Bancroft.

Méthodes de Calorimétrie. *Usitées au Laboratoire Thermique de l'Université de Moscou par W. Louguinine et A. Schukarew. Traduit de la Russe par G. Ter Gazarian. 18 × 27 cm; pp. 192. Paris: A. Hermann. Genève: Georg & Co., 1908. Price: Linen, 8 francs.*—Ostensibly this is merely a book describing the methods of calorimetry in use at the Moscow laboratory but actually

it is a good deal more than that. When giving reasons for using this, that, or the other method, it is of course necessary to discuss general principles to a certain extent. It is distinctly interesting to learn that the Germans use thermometers with milk-glass scales because they are unable to make such a glass that the zero of the thermometer will be fairly constant and that will permit the ruling of fine lines.

Although arranged as a book, the volume really is a series of essays by one or the other of the authors. There are fourteen of these essays or chapters and they are well worth reading though the reviewer feels that the effectiveness of the book would have been increased if there had been less doubt whether the subdivisions were essays or chapters. *Wilder D. Bancroft*

The Chemical Constitution of the Proteins. *By R. H. Aders Plimmer. Monographs on Biochemistry. Edited by R. H. Aders Plimmer and F. G. Hopkins. Part I. 15 × 24 cm; pp. xii + 100. Price: $1.00 net Part II. 15 × 24 cm; pp. viii + 66. Price: $0.80 net. New York: Longmans, Green & Co., 1908.*—In the preface the author says: "The substance Protein, which constitutes the most important part of the material basis of all animal and vegetable life, has naturally attracted the attention and energy of numerous investigators throughout the past century. Progress in the study of this subject, on account of its difficulty, has been exceedingly slow, and it is only of recent years that the discovery of new methods by Emil Fischer has enabled us to increase our knowledge to its present extent. By these methods we have been able to advance from the conception of "albumin" to its actual separation into numerous units, and also to determine their arrangement in the molecule. On this account a monograph embodying the results of the most recent investigations, together with their connections with the work of the other and earlier investigators, needs no excuse for its appearance, as the subject is now being studied in every direction."

In the first volume which treats of the chemical composition of the protein molecule and the chemical constitution of its units, the subject is taken up under the headings: the monoamino acids; the diamino acids; monoamino-monocarboxylic acids; monoamino-dicarboxylic acids; diamino-monocarboxylic acids; heterocyclic compounds; the optically active amino acids. The second volume treats of the synthesis of the proteins and the headings are: the condensation together of amino acids; the biuret base; the linking together of amino acids; the polypeptides. Each volume has its own bibliography and the two give a satisfactory and useful outline of this important subject.

Wilder D. Bancroft

The Chemisty and Literature of Beryllium. *By Charles Lathrop Parsons. 14 × 22 cm; pp. iv + 180. Easton: Chemical Publishing Co., 1909.*—In the preface, the author says: "This book is written with the main object in view of saving preliminary study and labor to future investigators of beryllium and to point out some of the peculiarities of this interesting element which are apt to lead the novitiate toward erroneous conclusions. Especially is it desired to call attention to the fact that a large proportion of its credited compounds are in reality but indefinite solid solutions. This condition of the literature of beryllium is due to the abnormal extent to which its hydroxide is soluble in

solutions of its normal salts, giving rise to solids of almost any degree of basicity or to solutions with decreased osmotic effects. Accordingly, results of analysis, freezing points, etc., give little evidence of the true nature of its compounds, unless accompanied by proved definiteness of composition, a proof too often omitted throughout the whole field of inorganic chemistry, but nowhere more than in studying beryllium and its compounds.

"More labor has been expended upon the bibliography than its limited extent may seem to indicate. It is believed that it will be found to contain references to all or nearly all the original articles on beryllium and that the reference to abstracts will also be found fairly complete through 1902. Since 1902 the original articles and chief abstracts have alone been entered. It has been deemed advisable to include a brief abstract, at times critical in tone, of each article, but it is not claimed that these abstracts always cover the full subject matter of the original, although nothing important is intentionally omitted."

Monographs of this sort are extremely valuable and this one is no exception. The author was well qualified for the task. He has given us what is probably the best determination of the atomic weight of beryllium and his use of the methods of physical chemistry has enabled him to bring order out of the chaos of alleged basic salts. *Wilder D. Bancroft*

The Elements of Physical Chemistry. *By J. Livingston R. Morgan. Fourth edition, revised and enlarged. 12 × 19 cm; pp. xiv + 539. New York: John Wiley & Sons. London: Chapman and Hall, 1908. Price: $3.00.*—In this new edition we find references to the work of Mills on the heat of vaporization; to that of Morgan and Stevenson on surface tension; to Hawley's work on white lead and Cox's on chromates; to the work of Bell and Taber on the copper sulphates; to that of Moore and Frazer on osmotic pressures; to that of Luther and McDougal on reaction velocity; to Osaka's work on ionization of weak acids; and to Noyes's work on the temperature coefficient of ionization.

Stress is laid on the electrolytic separation of metals by graded electromotive forces, p. 473; but the student is left to struggle for himself with the theory of electrolytic separations as actually made. The reviewer notes with sorrow the unjustifiable spelling of 'cathion.'

A curious point of view crops up on p. 183 where the author says:

"As this theory [of electrolytic dissociation] to-day is much misunderstood by many, and is the subject of much speculation on the part of others, it will be necessary for us to consider carefully just what is fact and what assumption, and to see clearly which portions are hypothetical, and which are destined to remain under any hypothesis or lack of hypothesis; in other words which are experimental facts. It may be said however that that which is hypothesis in this theory is unessential, as far as the use of the data is concerned, and the only hypothesis present, as we shall consider it, is that inherent in the terminology, which is a relic of the atomistic hypothesis and so utterly beyond our power to prove or disprove.

"The salient facts which have been grouped in this theory, *for it is a theory in the sense that it is a law of nature holding between certain limits*, although these are not as yet definitely fixed, are as follows:....."

The italics are mine. To me this seems to be either a new definition of a theory or of a law of nature. *Wilder D. Bancroft*

EQUILIBRIUM IN THE SYSTEM, SILVER CHLORIDE AND PYRIDINE

BY LOUIS KAHLENBERG AND WALTER J. WITTICH

No work has hitherto been done on compounds of silver chloride and pyridine. Several salts of silver with pyridine of crystallization have been studied by Jorgensen,[1] Schmujlow,[2] Lincoln,[3] Klobb,[4] Varet,[5] and Kahlenberg,[6] but compounds of silver chloride and pyridine have not been described thus far.

The object of this work is to study the system silver chloride, pyridine in the light of the phase rule.

The pyridine used for this purpose was a Merck's preparation. It was dried several days over fused caustic potash and then distilled. The fraction passing over between 114° C and 115° C under a barometric pressure of 741.5 mm was used. The silver chloride was made from Merck's silver nitrate, which was fused and pulverized in the dark, dissolved in hot water and precipitated with hydrochloric acid. The precipitated silver chloride was washed thoroughly until no trace of hydrochloric acid could be detected in the filtrate. It was then pressed between porous plates and dried in an air bath at a temperature of 150° C. After several hours of drying, the silver chloride was pulverized and redried to remove all traces of moisture. All of this work was done in the dark.

The solubility determinations were performed with the Meyerhoffer and Saunders[7] apparatus consisting of a hard glass tube, fitted with a spiral stirrer, the whole being immersed in a constant temperature bath. An ordinary water bath was used for the determinations from 0° to 60° C. From

[1] Jour. prakt. Chem. (2), **33**, 502 (1880).
[2] Zeit. anorg. Chem., **15**, 23 (1897).
[3] Jour. Phys. Chem., **3**, 469 (1899).
[4] Bull. Soc. Chim., Paris (3), **11**, 605 (1894).
[5] Ibid. (3), **5**, 843 (1891).
[6] Jour. Phys. Chem., **3**, 386 (1899).
[7] Zeit. phys. Chem., **28**, 464 (1899).

60° C up to 110° C a paraffine bath proved most efficient in the maintenance of a constant temperature. For the determinations from 0° C to —10° C a freezing mixture of calcium chloride and ice was used, while from —10° C to —20° C a mixture of ice and equal parts of sodium chloride and calcium chloride was employed. From —20° C to —60° C solid carbon dioxide and ether were used. The temperatures below zero were read on a toluene thermometer which permitted estimations to tenths of a degree. An ordinary mercury thermometer graduated to tenths of a degree was used for the upper register. From 0° C to 110° C the determinations were made at temperature intervals of ten degrees. Below zero this was impossible; the temperature intervals varied.

The solvent and salt were stirred together for an hour and a half and in some cases two hours, in order to assure equilibrium. To test whether equilibrium had been reached, some of the liquid was removed at different intervals of time, by means of a pipette, and the silver content determined. The nozzle of the pipette was capped with muslin in order to hold back any crystals.

Owing to the insolubility of silver chloride in both water and the mineral acids, no volumetric method of analysis could be used. The addition of water or acid to the sample liquid caused silver chloride to separate from the solution. Consequently a gravimetric method of analysis was used. The sample was drawn from the tube with a pipette as stated, transferred to a weighing bottle and weighed. The liquid was then transferred to a beaker, diluted with distilled water and the silver chloride precipitated by adding dilute nitric acid. After boiling and allowing to stand over night, the silver chloride was transferred to a Gooch crucible and thoroughly dried at 150° C in an air bath. The drying was continued until the silver chloride was of constant weight. All these operations were performed in a dark room.

The experimental results recorded in the following table are the average of two or more concordant determinations. Owing to the difficulty of maintaining constant temperature

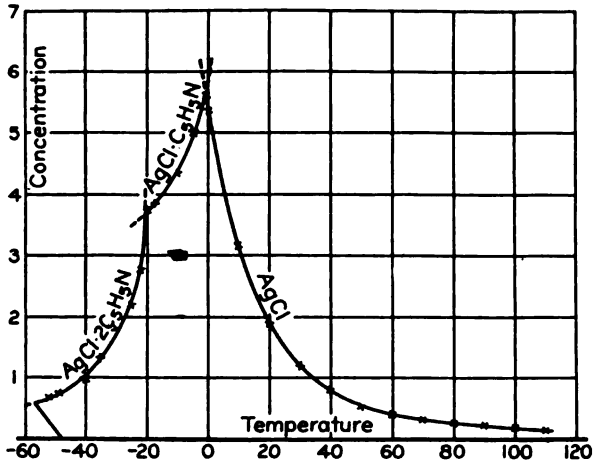
below 0° C, repeated determinations were made. Judging from the smoothness of the curves the results cannot be far from the true ones.

The experimental results obtained are given in the following table:

Equilibrium between saturated solution and solid.
$AgCl.2C_5H_5N$

Temperature °C	Grams AgCl in 100 grams of pyridine
—57 Freezing point of saturated solution	—
—52	0.70
—49	0.77
—40	—
—35	0.99
—30	1.36
—25	1.80
—22	2.20
transition point	2.75
Equilibrium between saturated solution and solid. $AgCl.C_5H_5N$	
—20	3.71
—18	3.85
—10	4.35
—5	5.05
—1	5.60
transition point.	—
Equilibrium between saturated solution and solid AgCl.	
0	5.35
10	3.17
20	1.91
30	1.20
40	0.80
50	0.53
60	0.403
70	0.32
80	0.25
90	0.22
100	0.18
110	0.12

The results in the table are shown graphically in the accompanying figure. The temperatures are plotted as abscissae, and the amounts of silver chloride in 100 grams of pyridine as ordinates.



At —56° C salt and solid pyridine separate out together, and on lowering the temperature the entire mass congeals. We have then at —56° C a quadruple point; the non-variant system, consists of four phases: solid pyridine, solid salt, saturated solution, and vapor which are in equilibrium with one another. The solubility gradually increases from —56° to —22° C. The solid in equilibrium with the saturated solution between the said temperatures has the composition $AgCl.2C_5H_5N$. These crystals are minute and very unstable at temperatures above —22° C. The analysis of the crystals yielded 54 percent pyridine while the calculated amount is 52 percent. The somewhat high experimental result is probably due to adhering pyridine, for it is practically impossible to dry the crystals thoroughly owing to their instability.

From —20° C to —10° C the solubility curve takes a different course. The solid which is now in equilibrium with the saturated solution has the composition $AgCl.C_5H_5N$.

The crystals are minute and needle-like, and upon analysis they were found to contain 34.2 percent pyridine. The formula $AgCl.C_5H_5N$ represents 35 percent pyridine. Between —22° C and —20° C we have then a transition point at which the four phases, vapor, saturated solution, $AgCl.2C_5H_5N$ and $AgCl.C_5H_5N$ are in equilibrium.

The crystals of $AgCl.C_5H_5N$ are much more stable than those of $AgCl.2C_5H_5N$ and can easily be dried between porous plates.

Between —1° C and 110° C the curve takes a most remarkable course. One would naturally expect the solubility curve to continue going up, but from —1° C to 110° C the solubility steadily decreases. When the melting point of the compound $AgCl.C_5H_5N$ has been passed, the solid phase again changes and we now have AgCl. Consequently —1° C is another transition point at which the phases, vapor, saturated solution, $AgCl.C_5H_5N$ and AgCl are in equilibrium. Upon a further rise in temperature the AgCl gradually drops out of solution until at 110° C the solubility has decreased to 0.12 percent.

Summary

The results of this new work show that there are two distinct crystalline compounds of silver chloride and pyridine. The two compounds are: $AgCl.2C_5H_5N$ and $AgCl.C_5H_5N$, hitherto unknown. The $AgCl.2C_5H_5N$ occurs between the temperatures —56° C and —22° C. It appears in the form of minute crystals which are very unstable at temperatures above —22° C. The $AgCl.C_5H_5N$ occurs between the temperatures —20° C and —1° C. This salt consists of minute needle-like crystals which are more stable than the $AgCl.2C_5H_5N$.

It is most interesting to note that the solubility of the AgCl decreases from —1° C to 110° C as the temperature rises. The entire equilibrium curve in the system chloride and pyridine has thus been established from the freezing point of pyridine up to 110° C.

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A SIMPLE METHOD FOR DETERMINING VAPOR DENSITIES

BY PHILIP BLACKMAN

PART IX[1]

The two equations given in the Journal of Physical Chemistry, 12, 670 (1908), can be converted into the single simple equation given on page 676 (Ibid.) in the following manner.[2] On page 670 replace w_1, w_2, throughout by x_1, x_2, respectively; then the respective equations become

$$d_1x_2 + d_2x_1 = \frac{d_1d_2pLV(L_c - l)}{31068\, lL_c(273 + t_1)},$$

and $x_1 + x_2 = w$.

Since $x_2 = w - x_1$, the first equation may be written

$$d_1(w - x_1) + d_2x_1 = \frac{d_1d_2pLV(L_c - l)}{31068\, lL_c(273 + t_1)},$$

which, on multiplication throughout by the factor $100/w$, becomes

$$d_1\left(100 - \frac{100x_1}{w}\right) + d_2\left(\frac{100x_1}{w}\right) = \frac{100d_1d_2pLV(L_c - l)}{31068\, wlL_c(273 + t_1)}.$$

But $(100x_1/w)$ represents the percentage by weight of the component x_1 and let it be written w_1; and $\left(100 - \frac{100x_1}{w}\right)$ that of the second constituent, which is now equal to w_2 or $100 - w_1$, therefore

$$d_1(100 - w_1) + d_2w_1 = \frac{100\, d_1d_2pLV(L_c - l)}{31068\, wlL_c(273 + t_1)}.$$

There is not the slightest need for using thick-walled or Jena tubing from which to make the bulb; any kind of tubing (of not too thin walls) will do perfectly well, and is moreover very easy to seal up or open. The author invariably

[1] Continued from Jour. Phys. Chem., 13, 143 (1909).

[2] Cf. Zeit. phys. Chem., 65, 550 (1909).

used ordinary glass tubing of wall-thickness not exceeding 1.5 mm.

It has already been pointed out that there is not the slightest need for using a graduated capillary tube for manometer, as L, L_c, and l can very easily be measured by the aid of a mm measure, compass, dividers, or callipers. However, should anyone still desire to use a graduated tube, there is no necessity whatever to go to the trouble of making one, as the graduated stem of a disused thermometer will do quite well for the purpose. It is quite immaterial whether L, L_c, and l are measured in mm, inches, or any other unit of length (provided one unit only is used throughout); this will be at once evident from the formula

$$\frac{31068\, wlL_c(273 + t_1)}{pLV(L_c - l)},$$

where the factor

$$\frac{lL_c}{L(L_c - l)}$$

plainly from its nature is simply a numerical quantity.

It is the author's opinion that in the special apparatus described and figured on page 678 a hollow stopper would much better withstand heat than a solid one.

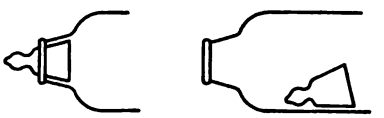

Fig. 1

The following is a brief, clear summary of the essential consecutive steps in the performance of an experiment. A clean tube has one end closed. The manometer is prepared, cooled down to room temperature, and L measured. The manometer and weighed quantity w of substance to be experimented on are introduced into the tube. The tube is now sealed, allowed to cool to room temperature, and L_c measured. The room temperature t_1 and atmospheric pressure p are determined. The apparatus is next heated to

t_2 and l measured. The bulb is finally opened and V determined, and the necessary calculations effected.

Interesting variations for the method of obtaining the necessary formula for calculating vapor-density will be found in the Chemical News, **99**, 87 (1909).

PART X

Preparation of Manometer

The methods here described for preparing the pressure-gauge or manometer will be found much easier and more convenient than that previously detailed by the author, and they possess the additional advantages that the mercury-thread can be placed in any desired position and may be made of any required length.

(1) If the bore of the capillary-tube be very narrow, a piece of rubber tubing is pushed over one end, and a thread of mercury of required length is sucked in at the other end and drawn in till it reaches a convenient position near the rubber-fastened end, when the rubber tubing is immediately closed with a clip or pinchcock; the other end of the capillary-tube is sealed off in the flame, and the rubber-tube opened and finally removed.

(2) If the bore of the capillary-tube is not too narrow, one end of the tube is sealed off. A piece of glass tubing is softened in the flame and drawn out to a long, straight, fine (narrow) capillary-tube (see Fig. 2). This is filled with a drop of mercury, inserted in a horizontal position into the capillary-tube until its end reaches the desired position within the bore, and by gently raising the two tubes into an upright or a semi-vertical position a thread of mercury of the required length will run into the capillary-tube, after which the filling-tube is taken out.

Fig. 2

New Apparatus for Liquids

A capillary-tube, 30 to 40 cm long (the longer the better) with not too narrow a bore has one end sealed up and a mercury-thread inserted somewhere near the middle of it as is

described under "Method 2" above. A short thread (3 to 5 mm in length) of the liquid whose vapor-density is to be determined is put into the bore 3 or 4 cm away from the mercury-thread. The length L of the air-thread enclosed between the mercury-thread and the sealed end is measured, and also the length δ of the thread of liquid is determined (see Fig. 3). By the aid of an ordinary magnifying-glass it should be possible to measure δ to fourths or even fifths of a mm. The other, open end of the tube is now sealed off, and when it has had time to cool down to room temperature the length L_c of the manometric air-thread (*i. e.*, between the mercury-thread and the sealed end on its side) is measured (see Fig. 4).

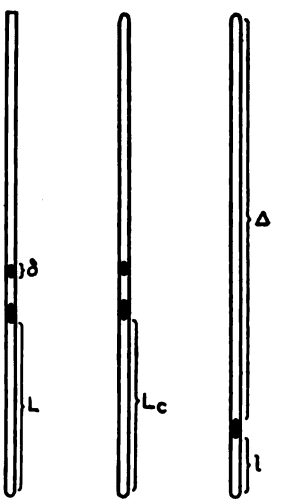

Fig. 3 Fig. 4 Fig. 5

The tube is heated to a temperature sufficiently high to vaporize completely the enclosed substance (either by means of a heating-jacket and the vapor from a suitable boiling liquid, or better in a thermostat containing a heating-medium such as glycerin or paraffin-wax). The vaporizing-temperature will generally have to be very high, much higher than the temperature at which the substance vaporizes at ordinary atmospheric pressures, because the pressures within the

capillary-tube are very great. For this same reason, any liquid which decomposes at high temperatures cannot be experimented upon with this apparatus. When the mercury-thread has become stationary the length l of the manometric air-thread is measured, and also the length δ of the bore of the capillary-tube occupied by the vapor of the substance is determined (see Fig. 5).

The room-temperature t_1 and the atmospheric pressure p are measured.

(In very accurate work allowance must be made for the concavity of the ends of the substance when measuring δ; the correction however is very small and may for all ordinary purposes be neglected).

The specific gravity s (as measured on the metric-system) of the substance experimented upon must be determined at the temperature of the measurement of δ.

Let α = the area of the cross-section of the bore of the capillary-tube (α is not required to be known); then the weight of the substance $= s\delta\alpha$, and the volume of the vapor $= \Delta\alpha$; substituting these quantities for w and V respectively in the formula hitherto used, the formula to be employed in the calculation of vapor-densities with this apparatus is

$$d = \frac{31068\, s\delta l L_c(273 + t_1)}{pL\Delta(L_c - l)}.$$

It will be noticed that with this apparatus consideration of H, n, is entirely absent[1] and thus the formula just quoted is quite correct.

The apparatus should not be used with substances which act upon mercury.

This method may not be found so accurate as the ones previously described by the author, but it is nevertheless exceedingly interesting both from practical and theoretical points of view.

When the tube is being finally sealed up, it will be found that the warmth from the hand and the heat from the sealed

[1] See Zeit. phys. Chem., **63**, 49 (1908).

end are able to cause the enclosed air in the bore to exert a sufficiently great pressure to distend the bore at the softened, sealed end and very often to blow a hole through that part. The author could discover only one way of preventing this. The other sealed end is pushed into a cork, by which the tube is to be clamped while it is being sealed (see Fig. 6). When the softened end has closed in the flame, the tube, while still being held in the flame, is rubbed with a piece of filter-paper or blotting paper moistened with some volatile liquid; the cooling effect of this will generally repress the expansive force of the contained air, and enable the end to be well sealed off and annealed. This cooling process must be continued some little time after the tube has been removed from the flame, until the soft end has had time to solidify. These operations will be found the most difficult part of the experiment, and on it more than on any other will depend the success of a determination.

Fig. 6

The tube may be heated to $t°_2$ in an upright (vertical) position if desired, for the internal pressure is so great that the weight of the mercury-thread is of negligible effect upon the column of air (see the observation upon this question in the Zeitschrift für physikalische Chemie, **63**, 51 (1908)).

Substance	s	δ mm	l mm	L mm	L_c mm	p mm	t_1 °C	Δ mm	d Found	d Theory
$(C_2H_5)_2O$	0.7312	3.5	33	129	135	746	15	304	35.1	37.0
$CO(CH_3)_2$	0.7996	2.25	42	131	147	751	14	298	32.6	29.0

Errata

Page 661. The footnote should refer not to the title, but only to Part I. Only Part I was read before the London Chem. Soc.

Page 662, line 14; instead of "Hh" read "H, h."

Page 670, line 1; instead of "let w, w_2" read "let w_1, w_2."

Page 670, line 5; instead of " or = " read " or ϕ = ".

Page 672, line 30; instead of "need, whatever, to" read "need whatever to."

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A NEW METHOD FOR DETERMINING VAPOR-DENSITIES

BY PHILIP BLACKMAN

PART VII[1]

A wide tube is closed at one end A, and the open end is drawn out to a nozzle B, just wide enough to allow a small glass-stoppered weighing-bottle to pass through it. A permanent line is marked on the tube some distance away from the closed end A, and the volume of the tube from A to the mark is determined once for always and the value (v) marked permanently on the glass.

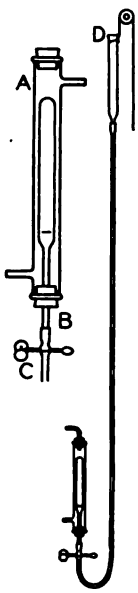

Fig 1.

A piece of rubber pressure-tubing, several metres long, has one end C closed with a clip or pinchcock, and the other end fitted with a glass tube D about 1 metre in length. The tube D is kept upright, and dry, clean mercury is poured in until both rubber tube and D are filled; both are agitated to remove all air-bubbles.

The weighed quantity (w) of substance to be experimented on is introduced into the measuring-tube AB, the end C of the rubber tube fastened onto B, AB placed vertically with A to the top, D fixed high up in an upright position, the pinch-cock or clip opened and the mercury in AB brought to the mark by raising or lowering D, the difference (m_1) in height between the mercury levels measured, AB surrounded by a suitable heating-jacket and heated in the vapor of some substance boiling well above the temperature at which the substance experimented on vaporizes at 760 mm pressure, and D further raised (or else mercury poured into it) to maintain the mercury in AB

[1] Continued from Jour. Phys. Chem., 12, 692 (1908); Ber. chem. Ges. Berlin, 41, 441 (1908).

at the mark. The difference (m_2) in height between the mercury levels is now ascertained, the external temperature (t_1) and pressure (p) determined, and the necessary calculation effected by means of the formula

$$\frac{31068\,w(273 + t_1)(273 + t_2)}{v[(p + m_2)(273 + t_1) - (p + m_1)(273 + t_2)]}.$$

(t_2 = the temperature of the heating medium).

It must be remembered that the volume of the weighing bottle should be subtracted from v before proceeding with the calculation of the result.

This apparatus may not be found as simple or convenient to manipulate as those described in Part VI, but it possesses these advantages over those detailed in Parts I–IV (Journal of Physical Chemistry, **12**, 679 688 (1908)): (1) the determinations are always carried out at constant volume; and (2) the measuring tube AB can be made as small as one pleases, thus reducing the combined dimensions of the measuring-tube and heating-jacket to a small compass. (For instance, for a permanent measuring capacity of 50 cc, the combination need not occupy a bulk more than 30 cm by 4 cm). Some difficulty may be encountered in fixing, raising, and lowering D, on account of the fairly considerable length of CD; but a piece of string fastened to D and passed over some form of support fixed high up should quite easily facilitate the matter. The measuring of m_1 and m_2 may also present some little inconvenience for the same reason; generally however m_1 will not exceed 80 cm, and if w be a moderately small quantity m_2 will rarely be greater than 2 metres.

PART VIII[1]

The simple equation given on page 689 (Journal of Physical Chemistry, **12** (1908)) can be derived from the two equations given on page 688 (Ibid.) as here shown.

On page 688 let w_1, w_2, throughout be replaced by x_1, x_2, respectively, and the equations then become

[1] Cf. Ber. chem. Ges. Berlin, **41**, 2487 (1908).

$$d_2x_1 + d_1x_2 = \frac{d_1d_2[v_2(p_2 \pm m_2)(273 + t_1) - v_1(p_1 + m_1)(273 + t_2)]}{31068\,(273 + t_1)(273 + t_2)}$$

and $w = x_1 + x_2$.

As $x_2 = w - x_1$, the first equation can be written

$$d_2x_1 + d_1(w - x_1) = \frac{d_1d_2\{v_2(p_2 \pm m_2)(273 + t_1) - v_1(p_1 + m_1)(273 + t_2)\}}{31068\,(273 + t_1)(273 + t_2)}.$$

Let this last equation be multiplied right through by the quantity $100/w$, and the result is

$$d_2\frac{100x_1}{w} + d_1\left(100 - \frac{100x_1}{w}\right) = \frac{100d_1d_2\{v_2(p_2 \pm m_2)(273 + t_1) - v_1(p_1 + m_1)(273 + t_2)\}}{31068\,w(273 + t_1)(273 + t_2)}.$$

But $100x_1/w$ is the percentage composition of one component, and $100 - 100x_1/w$ is that of the other constituent; if these quantities be respectively written as w_1, w_2, the equation takes the form

$$d_2w_1 + d_1(100 - w_1) = \frac{100d_1d_2[v_2(p_2 \pm m_2)(273 + t_1) - v_1(p_1 + m_1)(273 + t_2)]}{31068\,w(273 + t_1)(273 + t_2)}.$$

Corrigenda

Page 680, line 26; instead of "$p_1 = p_2$" read "$p_1 = p_2$)."

Page 680, line 29; instead of "v_2, volume" read "v_2 — volume."

Page 687, line 21; instead of "A and (*f*)" read "A, and (*f*)."

Page 688, line 4; instead of

"$1160\left(\frac{w_1}{d_1} + \frac{w_2}{d_2}\right)$;" read "$1116o\left(\frac{w_1}{d_1} + \frac{w_2}{d_2}\right)$;".

Page 690, line 30; instead of "ninth, and eleventh" read "and ninth."

Page 725, line 13; instead of "651" read "661."

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FRACTIONAL PRECIPITATION FROM SOLUTION

BY PHILIP BLACKMAN

If a substance be dissolved in a liquid and another used to precipitate it, then more of the substance by weight can be precipitated from the solution by using the other liquid in portions than by employing it all in one precipitating operation.

Let

W = the weight of the dissolved substance,

v_1, v_2 = the volumes of the precipitate and of the solvent respectively,

s = the coefficient of solubility of the substance in the solvent,

p = the coefficient of precipitability of the solute by the precipitant (*i. e.*, the quantity precipitable by unit volume of the precipitating liquid).

I. If the operation of precipitation be performed by using the total volume, v_1, of the precipitating liquid, then, if w be the weight of the solute precipitated, $W - w$ is the weight of the solute remaining, and

$$\frac{w}{W - w} = \frac{v_1 p}{v_2 s} \text{ or } w + w\frac{v_1 p}{v_2 s} = W\frac{v_1 p}{v_2 s}.$$

Hence:

$$w = \frac{v_1 p}{v_2 s} W \Big/ \left(1 + \frac{v_1 p}{v_2 s}\right) \quad \ldots\ldots\ldots\ldots\ldots (1).$$

II. If the precipitating process be carried out in n operations, employing each time the volume v_1/n of the precipitant, then the successive weights, w_1, w_2, $w_3 \ldots\ldots\ldots w_n$, of the solute precipitated will be:

$$w_1 = v_1 p(W - w_1)/n.v_2 s,$$
$$w_2 = v_1 p(W - w_1 - w_2)/n.v_2 s,$$
$$w_3 = v_1 p(W - w_1 - w_2 - w_3)/n.v_2 s,$$
$$\ldots = \ldots\ldots\ldots\ldots\ldots\ldots$$
$$w_n = v_1 p(W - w_1 - w_2 - w_3 - \ldots\ldots\ldots\ldots - w_n)/n.v_2 s.$$

Thus the total weight precipitated in the n operations

$$= w_1 + w_2 + w_3 + \ldots\ldots\ldots\ldots + w_n$$

$$= \frac{v_1 p}{n.v_2 s}\,(nW - nw_1 - \{n-1\}w_2 - \{n-2\}w_3 - \{n-3\}w_4 - \ldots\ldots\ldots\ldots - w_n)$$

$$= \frac{v_1 p}{v_2 s}\,W - \frac{v_1 p}{v_2 s}\,(w_1 + w_2 + w_3 + \ldots\ldots\ldots\ldots) + \frac{v_1 p}{n.v_2 s}\,(w_2 + 2w_3 + 3w_4 + \ldots\ldots\ldots\ldots).$$

Consequently

$$(w_1 + w_2 + w_3 + \ldots\ldots\ldots\ldots) + \frac{v_1 p}{v_2 s}\,(w_1 + w_2 + w_3 + \ldots\ldots\ldots\ldots)$$

$$= \frac{v_1 p}{n.v_2 s}\,(w_2 + 2w_3 + 3w_4 + \ldots\ldots\ldots\ldots) + \frac{v_1 p}{v_2 s}\,W.$$

Therefore:

$$w_1 + w_2 + w_3 + \ldots\ldots\ldots\ldots + w_n$$

$$= \text{the total weight precipitated}$$

$$= \frac{\frac{v_1 p}{v_2 s}\,W}{\left(1 + \frac{v_1 p}{v_2 s}\right)} + \frac{\frac{v_1 p}{n.v_2 s}\,(w_2 + 2w_3 + 3w_4 + \ldots\ldots)}{\left(1 + \frac{v_1 p}{v_2 s}\right)} \quad \ldots\ldots (2).$$

Equation (2), it will be observed, exceeds Equation (1) by the quantity

$$\frac{v_1 p}{n.v_2 s}\,(w_2 + 2w_3 + 3w_4 + \ldots\ldots)\Big/\left(1 + \frac{v_1 p}{v_2 s}\right)$$

which proves the above statement.

The preceding algebraic method of procedure (compare "Solution: Fractional Extraction" by the author in the Chemical News, 93, 72 (1906)) is especially interesting in view of Ostwald's statement in his "The Scientific Foundations of Analytical Chemistry" (English Translation, 1908 Edition, page 18) to the effect that the solution of the problem requires the aid of the calculus.

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A GRAPHITE CATHODE DISH

BY J. W. TURRENTINE

In conducting a laboratory course in applied electrochemistry, one devoted largely to that phase of electrochemistry which has to do with solutions and the electrolysis of solutions, the need has been experienced for some good material which could be substituted for platinum in the construction of insoluble electrodes. Platinum, to be sure, makes the ideal insoluble electrode, but its cost makes the matter of supplying a large class with electrodes constructed of it impracticable. The initial expense is great and the care of it is a burden on the instructor.

In the Cornell laboratories, for ordinary work graphite has been substituted. Trouble was experienced with this material on account of the fact that it was porous and absorbed the solutions in which it was used and therefore could not be cleaned readily. This prevented its use in experiments where the impurities might interfere with the desired reaction. Also, at high current densities, the graphite electrodes showed a tendency to disintegrate and to fill the solution with clouds of finely divided graphite powder. This was due, possibly, to the discharge within its pores and beneath its surface of gases which forced off the surface particles. A further objection was found in the graphite's propensity for rubbing off and smutting.

After experimentation to determine a means of preventing the absorption of solutions by the graphite, it was found that if the graphite electrodes were treated while hot with molten paraffine, in amounts which are readily absorbed by them, the surface of the graphite acts as though it were greased and is not wetted by aqueous solutions. Because of surface tension phenomena, the pores are not entered by the solutions. This treatment, by keeping solutions from the pores, should also prevent the disintegration of the electrodes at high current densities; however, whether it does or

not has yet to be determined. Certainly it does not when the graphite is made anode in chloride solutions, but here we have the paraffine attacked by the evolved chlorine and naturally its efficiency as a protective agent is diminished. The treatment with paraffine furthermore reduces to a minimum the inclination of the graphite to rub off, so that it is rendered quite clean and it may then be handled freely without smutting.

When mention was made to the Acheson Graphite Company of the behavior of the graphite when thus treated, it was found that they have employed the same means for improving their electrodes when designed for certain purposes.

In the Wesleyan laboratory we are now using graphite electrodes made from the Acheson sheet graphite of 0.5 cm thickness. The sheet is cut into pieces which are 15 cm by 2.5 cm in dimensions. One end is copper plated and a copper wire about 20 cm long is twisted around this end and is soldered in place to the copper plate. To protect the exposed metal at this point from fumes, the end of the electrode is covered with a light coating of varnish. The graphite is then paraffined, while hot. The electrodes are supported by a very simple device which consists merely of a block of wood of sufficient size to rest across the top of a beaker. It contains two parallel slits, 2.75 cm apart and of the proper width to admit the electrodes and to hold them snugly in position.

We were thus enabled to supplant very satisfactorily by the use of paraffined graphite the platinum sheet electrodes heretofore used in the ordinary experiments in the laboratory work. In electrochemical analysis, however, and separations, expediency still demanded the use of the Classen platinum dish.

The use of a graphite dish as a substitute for the platinum dish need not be confined to pedagogic electrochemistry, but should also find an extended use in commerical laboratories.

Recent developments in the field of electrochemical

analysis, due to the important work of Professor E. F. Smith and students and other investigators, have afforded us many beautiful methods of electrochemical analysis which might well and should be used in industrial laboratories. This is especially true of those laboratories connected with metallurgical plants where some electrochemical methods are already in use. The substitution of the very rapid new methods for those already in vogue, requiring hours for precipitations and separations which could be accomplished in a few minutes if accompanied by effective stirring, would perhaps recommend itself to the works chemist if this substitution could be made without the very considerable outlay now necessary for platinum electrodes. The very convenient Classen dish is not essential to the equipment requisite for electro-analysis, yet it is almost a necessity; one's equipment is scarcely complete without a number of them. To provide them, however, requires a considerable outlay.

By changing from the old system of electrochemical analysis to the new a saving in the amount of platinum in use could undoubtedly be effected. The old system involves the use of the stationary, cylindrical, platinum cathodes, while the new methods depend on rotating electrodes, stirred solutions, the platinum dish and other devices for making possible the use of high current densities. The only points that can be produced in favor of the stationary electrode method is that the electrolysis can be started in the late afternoon and without further attention may be allowed to complete itself during the night, and that the multiplication of the number of analyses does not involve an equal increment in the time required for the operation. However, increasing the number of analyses does increase the number of electrodes which are necessary and therefore increases the cost for equipment. With a single rotating anode and Classen dish cathode the number of analyses could be made with a time expenditure of only a few minutes for each analysis and would require the attention of only a fairly expert chemist.

In equipping a new laboratory for electrochemical anal-

ysis it is clearly poor economy to install the antiquated apparatus, numerous stationary electrodes, in preference to the new, a much smaller number of rotating anodes and dish cathodes; and there are those who think, with reasons, that it is also poor chemistry.

If our contention is true that it is both good economy and good analytical chemistry not only to equip laboratories with the apparatus requisite for performing rapid analyses in stirred solutions, but also, if necessary, to discard present equipment of stationary electrodes in order to do so, then much more true is our contention if an apparatus constructed of a much less expensive material than platinum can be offered the profession.

Anticipating these advantages and encouraged by the success of the paraffined graphite electrodes, a graphite dish was prepared from a four inch, cylindrical stick of Acheson graphite. This dish was turned out on a lathe by Mr. G. B. Upton, of Sibly College, Cornell University, for whose great kindness I take this opportunity of expressing my sincere appreciation.

Graphite was chosen as the material of which to construct the dish because in it we have a substance which is at once a good conductor of the electric current, is cheap, is light in weight and is non-attackable by solutions. Its density is low, a little less than 2.2,[1] but varies from one electrode to another, and in different parts of a single electrode. With the density probably also varies the hardness, though the variation in both density and hardness is slight and gradual, so no difficulty on that account need be experienced in machining. Because of its low density, the walls of a dish may be made of sufficient thickness to lend strength and rigidity to the article without unduly increasing its weight.

The porosity of the graphite may prove to be the greatest obstacle in the way of the dish's becoming a success when

[1] FitzGerald: Trans. Am. Electrochem. Soc., Vol. II, 1909.

employed in the most accurate analysis. The degree of porosity is expressed numerically as the quotient obtained by dividing the difference between the real and apparent specific gravities by the real specific gravity.[1] The apparent specific gravity is that obtained when the interstices of the graphite are kept free of the liquid in which the determination is being made. This is accomplished by coating the sample lightly with shellac. The real specific gravity is found after the air has been removed from the pores of the sample by greatly reducing the pressure over the immersing liquid. When the suction is released the evacuated pores become filled. The average of several determinations gives the porosity of graphite at about 0.25. Such a degree of porosity would seem to make this substance an impossible one of which to construct a dish designed for such purposes as is this one. Very effective, however, is the paraffine in preventing the absorption of solutions into its pores. That the latter are not entirely filled by the paraffine is shown by the fact that alcohol is able to penetrate the paraffined graphite fairly readily. It is highly probable that while aqueous solutions do not enter the interstices, aqueous vapor does and condenses there to a certain extent; so it may be necessary eventually to fill these entirely with paraffine by the evacuation method used in the specific gravity determination.

The purity of graphite is high and therefore it is improbable that any contamination of solutions can possibly result from its use. It has been shown[2] that when a carbonaceous substance, like anthracite coal, has been graphitized, its impurities are almost completely volatilized, the more complete being the volatilization the higher the temperature of graphitization and the longer this heat is maintained. Graphite is then a very pure form of carbon and the Acheson product, in addition to its insolubility, has been shown[3] to be

[1] Fitzgerald: Trans. Am. Electrochem. Soc., Vol. II, 1909.
[2] Fitzgerald: Jour. Franklin Inst., Nov., 1902.
[3] Foerster: Zeit. angew. Chem., June, 1901.

very resistant to disintegration in solution. When made anode in caustic solutions, it is only very slightly attacked by the evolved oxygen. This is to be expected when we recall that the combustion point of some forms of graphite in oxygen is about 600° C.

Graphite is to be had of varying degrees of hardness, the harder varieties, while less pure, are more resistant to chemical action and undoubtedly would make a stronger and more durable article. Hardness would likewise enhance the possibilities for accurate and sharp machining, a fact to be borne in mind when choosing a graphite for the purposes described in this paper. Its tensile strength is about 80 percent of that of the carbon from which it is made, there being a deterioration of 20 percent in that property during the process of manufacture. With the combination of hardness and the above tensile strength it is possible to machine a dish whose walls are of very slight and uniform thickness, which thus possesses both strength and lightness in weight. The elasticity of the harder varieties of graphite is also worthy of note. Possessing these properties, there is no reason then why a graphite dish with proper use should not prove to be long lived to an entirely satisfactory extent.

The experimental dish was prepared for use by first burnishing on a revolving, steel-wire buffer, which served to remove all dust and gave the surface a somewhat polished appearance. The graphite still rubbed off on the fingers, but to a much lessened extent; after treating with paraffine it no longer rubbed off at all.

The dish was warmed in a hot air bath to a temperature of about 110°; while the dish was still hot molten paraffine was applied with a brush until it was no longer absorbed readily but remained visible on the surface. The dish was then returned to the oven, several sheets of filter paper were placed under it and the bath was maintained at the temperature of 110° for several hours. In this way the excess of paraffine was drawn off, by gravity and capillary action, into the filter paper. After this treatment the surface of the

graphite appeared quite dry. The dish was then reburnished.

The preliminary experiments conducted with this dish gave such very promising results that two other dishes were obtained through the esteemed courtesy of Messrs. Eimer & Amend, of New York. These are much lighter in weight, weighing respectively 38 and 32 grams after having been paraffined. Their capacity is 200 cc. In dimensions they are 9.5 cm in diameter across the top and are 5 cm deep. The lower part has the shape of a truncated cone, the conical shape beginning 2.5 cm from the upper edge and extending inward at such an angle that a flat bottom of 3.5 cm in diameter is afforded by the truncation. This shape was chosen so as to give a dish of straight sides. The walls are slightly less than 1 mm in thickness. The interior of the dishes presents a surface area of 54 square centimeters.

Another dish has been designed which is hemispherical in shape with the exception of a flattened portion of 3 cm in diameter on its bottom. Its dimensions are 9.5 cm in diameter across the top and 4.5 cm deep. The hemispherical shape has the advantage of affording the greatest capacity for the least wall area. As, of course, the weight of the dish lies in its walls, the smaller the area of the walls the less will be the weight. The hemispherical dish therefore gives the greatest capacity for the least weight.

The first experiments were made to determine the most satisfactory method for drying, attention being paid to speed as well as to accuracy. A method frequently used in drying the Classen dish with deposited metal is to wash with absolute alcohol and to burn off the excess. Applying the severest test first, this method of drying was used; the dishes were washed with distilled water, followed by absolute alcohol and the excess of alcohol was burnt off. After cooling in a desiccator the dishes were weighed.

Some of the results showed only a slight loss in weight while others showed a loss of almost 5 mg, due, no doubt,

as was found, to the loss in paraffine through being dissolved by the alcohol.

The method was then adopted of drying, after washing with distilled water, by holding the dishes by means of crucible tongs directly over the smokeless flame of a Bunsen burner, moving them around during the drying so that the heating would be uniform; they were then cooled in a desiccator. This extremely crude method was justified by its rapidity and gave surprisingly satisfactory results, as is shown by Table I.

TABLE I

Number	Weight before	Weight after	Loss
1	37.2660	37.2660	None
2	37.2660	37.2658	0.0002
3	37.2658	37.2652	0.0006
4	33.1400	33.1400	None
5	33.1400	33.1400	"
6	33.1400	33.1400	"

A number of determinations of efficiency were then made by electrolyzing an acidified solution of copper sulphate contained in a graphite dish in series with a copper coulometer filled with a portion of the same solution. Copper anodes were employed in both cells and a copper cathode in the coulometer. A current of 0.1–0.16 amperes was passed and the electrolysis was continued for about one hour in each run. Some of the results obtained are given in Table II.

TABLE II

Number	Cathode gain in coulometer	Cathode gain in graphite dish	Difference
1	0.1140	0.1128	0.0012
2	0.1582	0.1570	0.0012
3	0.1784	0.1770	0.0014
4	0.1748	0.1728	0.0020
5	0.2008	0.2004	0.0004
6	0.1924	0.1920	0.0004
7	0.1924	0.1924	0.0000
8	0.1772	0.1758	0.0012
9	0.1818	0.1802	0.0016
10	0.2126	0.2122	0.0004

An occasional result failed signally to agree with the theoretical value. As a check on the method, a Classen dish, containing a similar solution and copper anode was also placed in the circuit; this cell was electrolyzed in series with the other two. The platinum dish was dried with alcohol, the excess of which was burnt off, and was cooled in a desiccator. The results gotten with the Classen dish are shown in Table III.

TABLE III

Number	Cathode gain in coulometer	Cathode gain in Classen dish	Difference
1	0.1140	0.1142	0.0002
2	0.1084	0.1040	0.0044
3	0.1748	0.1768	0.0020
4	0.2008	0.2030	0.0022
5	0.1924	0.1919	0.0005
6	0.1772	0.1753	0.0019
7	0.1818	0.1807	0.0011

These results, as a whole, are hardly as good as those obtained with the graphite dish and, like those, an occasional one was bad. The errors observed in the case of the Classen dish are doubtless due to hurried and perhaps careless manipulation. It may be noticed, moreover, that in the case of the graphite dish the results are mostly low, while in that of the platinum dish they are sometimes high and sometimes low.

In Table IV the results obtained with the Classen dish are tabulated against those obtained with the graphite dish.

The results obtained for the graphite dish as set forth in this table are for the most part likewise lower than those obtained with the platinum dish. It appears that there is perhaps some loss in the weight of the dish itself in drying which causes the low results. Therefore, the method of drying directly over the flame will be abandoned and instead the dishes will be washed thoroughly with distilled water and then dried rapidly in a stream of warm, dry air.

TABLE IV

Number	Cathode gain in platinum dish	Cathode gain in graphite dish	Difference
1	0.1142	0.1128	0.0014
2	0.1040	0.1038	0.0002
3	0.1650	0.1642	0.0008
4	0.1768	0.1728	0.0040
5	0.2030	0.2031	0.0001
6	0.1919	0.1920	0.0001
7	0.1997	0.1974	0.0023
8	0.1753	0.1758	0.0005
9	0.1807	0.1802	0.0005
10	0.2125	0.2122	0.0003

The dishes are now being tested in actual analyses. Known volumes of a standard copper solution are being analyzed in them with rotating anode and at high current density. This will be considered the crucial test and not until the results of this test are known can the dish be unqualifiedly recommended. This paper is therefore merely a preliminary note. No further tests are needed, however, we feel, to show that it may be substituted profitably in numerous electrochemical operations where the Classen dish has been employed heretofore, or would have been had it been a less expensive article.

These dishes have been suggested for use in other operations not connected with electrolysis, such as digestions in hydrofluoric acid at high temperatures. In such cases the beaker shape would probably be advantageous.

A rotating graphite anode has been designed to accompany the dishes. This is constructed after the general plan of the platinum anode described by Miss Langness.[1] It is dish-shaped and contains radial slits in its walls and a circular opening in its bottom. It is hoped that by means of it the interesting results obtained with the anode referred to above may be duplicated.

Work is now being carried on, as intimated above, to

[1] Jour. Am. Chem. Soc., 29, 459 (1907).

show the limits of the graphite cathode dish.[1] A further report therefore will be made. The efficiency of the dish in numerous electrochemical separations and operations will also be determined. It is also our intention to investigate the rotating dish anode referred to above and a smaller, disc-shaped, rotating anode with a graphite stem.

Summary

(1) Simple, graphite electrodes are described which are designed for use in the place of platinum as insoluble electrodes in electrochemical experiments.

(2) An account is given of preliminary experiments with a graphite dish intended to supplant in some forms of electrochemical analysis the Classen platinum dish.

(3) The dish is recommended for electrochemical separations and for analyses where great accuracy is not required. Confidence is had that, after it has been further developed, it will be able to take the place entirely of the platinum cathode dish.

Wesleyan University,
April 1, 1909.

[1] Manufactured and on sale by Eimer & Amend, New York.

THE ELECTROCHEMISTRY OF LIGHT. VII

BY WILDER D. BANCROFT

The Theory of Solarization. Part I

In the preceding three papers, I have brought out the extraordinary differences of opinion in regard to the facts of solarization and the theories concerning them. As a basis for discussion, I give a list of certain conclusions drawn by various people in regard to the subject of photographic reversals. It must be recognized that some of the conclusions are mutually exclusive and that some of them are probably inaccurate. I have been very much pleased, however, to find that the differences and inaccuracies are more superficial than real, and that a slightly different wording of the conclusions will bring order out of what is apparently a hopeless chaos. So far as I can see, everybody has been more or less right and the trouble has been due largely to the failure to consider the field as a whole.

In the following list of conclusions, names are occasionally appended in parentheses. When this happens, it means that the men in question vouch for the facts or have held the opinions cited; but not necessarily that they have discovered the facts or originated the opinions.

(1) A reversal of the photographic image may be obtained with daguerreotype plates, with collodion plates, with gelatine plates, and with pure silver bromide. The reversal is, therefore, due primarily to a change in the silver salt and it is independent of the nature of the material, such as gelatine or collodion, in which the silver salt may be embedded. The nature of the gelatine or collodion, however, has a marked effect on the readiness with which reversal takes place.

(2) It is much easier to obtain a reversal with a gelatine plate than with a collodion plate, and it is quite difficult to obtain a reversal with pure silver bromide. Reversals

occur more readily with a coarse-grained gelatine emulsion than with a fine-grained one.

(3) A reversal of the photographic image may be obtained: by a prolonged exposure; by the antagonistic action of light of different colors (Herschel, Draper); by an exposure to white light followed by bathing in a solution of an oxidizing agent and exposure to the spectrum (Abney); by the use of stained plates (Waterhouse); by the action of white light during development (Sabatier, Nipher); by very slow development of an under-exposed plate (Guébhard); by addition of thiocarbamide, etc., to the developer (Waterhouse); by very short and very intense exposures with a subsequent short exposure to diffused light (Clayden, Wood); by cathode rays followed by sunlight[1] (Goldstein); by positive light of two intensities[1] (Goldstein).

(4) The stronger the developer and the longer one develops, the more easy it is to obtain a reversed image. Very slow development of an over-exposed plate will give a normal image. The latent reversed image is destroyed more rapidly than the latent normal image by bromine, nitric acid, ammonium persulphate, chromic acid, etc.

(5) With pure silver bromide collodion and chemical development, the reversal begins at approximately the same time as the visible blackening of the silver bromide; but with silver bromide collodion containing silver nitrate, visible blackening takes place long before a latent reversed image is formed (Eder).

(6) The visible blackening of the plate which causes the second reversal is probably due to the formation of allotropic or metallic silver.

(7) The reversal of the image is facilitated by oxidizing agents and prevented by reducing agents (Abney).

(8) Oxidizing agents and reducing agents have nothing to do with the reversal of the image. Halogen absorbers

[1] Goldstein studied the blackening of silver iodide and did not attempt to obtain images. It would be possible to obtain reversals and consequently the cases are included here.

prevent the reversal of the image if present during the exposure (Lüppo-Cramer).

(9) When a plate is exposed to light during development, the partially developed image acts as a screen, protecting the silver bromide below it (Seely).

(10) When a plate is exposed to light during development, it makes no difference whether the light falls on the plate from above or below. There is, therefore, no screening effect due to the partially developed image (Nipher, Trivelli).

(11) In most cases there is a simple quantitative relation between the original exposure and the amount of light necessary during development if the plate is to be brought into the 'zero state' (Nipher).

(12) The latent reversed image can be developed physically. If a plate is fixed first and then developed physically, we may get a normal image or a reversed one, depending on the conditions of the experiment.

(13) In the developed plate, the reversed image is chiefly in the lower layers.

(14) According to Eder, there are three images on an undeveloped over-exposed plate: a latent normal image, a latent reversed image, and a normal silver image. According to Homolka, there are two latent normal images.

(15) When a platinum electrode, coated with silver bromide, is dipped in a bromide solution and exposed to a moderate light, it becomes the cathode. When a stronger light is used, the platinum electrode will sometimes tend to become the anode.

(16) A film of silver iodide swells and clouds when exposed to light. No measurable change in chemical composition takes place, and the rate of clouding under the influence of light seems to be increased by the catalytic action of oxygen, iodine, etc. (Scholl).

(17) The substance forming the latent reversed image is a silver oxybromide of the general type $AgBr_xO_y$ (Abney, Eder).

(18) The oxidation hypothesis of Abney is absurd (Luppo-Cramer).

(19) There is no such thing as a latent reversed image. The phenomena are due to the regeneration of silver bromide.

(20) The latent reversed image is a reduction product of silver bromide (Lüppo-Cramer).

(21) The developable image consists of silver bromide and an α silver sub-bromide which is itself not reduced by the developer; but which acts as a catalytic agent, causing the developer to reduce the silver bromide. This α silver sub-bromide can be reduced by light to a β silver sub-bromide which is also not reduced by the developer but which has no catalytic properties. Reversal occurs when the α silver sub-bromide has been changed in the high lights very largely to β silver sub-bromide and this change has not taken place to any great extent in the shadows (Trivelli).

(22) The Waterhouse process with thiocarbamide in the developer gives pseudo-positives (Nipher).

Since the latent normal image is unquestionably a substance of variable composition[1] containing less bromine than silver bromide, the first question to be decided is whether the latent reversed image consists of silver, bromine and oxygen, or of silver and bromine only. In other words, we have to decide for or against Abney's theory or any possible modification of it. It must be admitted that most of the objections to Abney's theory are unsound and that a very strong case can be made out for it. Lüppo-Cramer contends that Abney is wrong in his statement that reducing agents prevent the reversal, because silver nitrate and sodium nitrite are not reducing agents and yet they are effective in preventing the reversal. Lüppo-Cramer says that these two substances act as they do because they are halogen absorbers. This is precisely the same quibble[2] which was made years ago in regard to chemical sensitizers. Since bromine is an oxidizing agent, any substance which destroys it is to that

[1] Weisz: Zeit. phys. Chem., **54**, 334 (1906).

[2] Lüppo-Cramer: Photographische Probleme, 140 (1907).

extent and for those conditions a reducing agent. It is entirely a question of definition as is shown by the fact that Abney himself states that potassium nitrite[1] is very effective in preventing the reversal of the image. As in the case of the chemical sensitizers, the whole difficulty disappears if we say that depolarizers prevent the reversal of the photographic image when present in the film in sufficient quantities during the exposure.

If we accept Abney's theory, a good many phenomena become intelligible at once. Oxidizing agents facilitate the reversal of the image and reducing agents check it. In the case of long exposure the bromine reacts with moisture in the film, forming hypobromous acid which oxidizes the latent normal image. Since acids increase the oxidizing power of an oxidizing agent, we see that acids must increase the tendency to reverse, a point which troubled Abney a good deal. Since the concentration and the oxidizing power of the hypobromous acid depend, under these circumstances, on the concentration of bromine, we shall consequently expect a greater tendency to reversal in a coarse-grained emulsion than in a fine-grained one where the bromine may be lost by diffusion. The difficulty in getting reversed images with pure silver bromide[2] might be due to the lack of moisture. This seems more probable when we reflect that Luggin[3] got marked reversal under conditions which involved high bromine concentrations and therefore relatively high concentrations of hypobromous acid.

This is very satisfactory as far as it goes, and we began our experiments with the firm conviction that some modification of Abney's theory would probably account for all the facts. The first shock came when it was found that a solution of pure hypobromous acid did not enable us to get satisfactory reversals even though the concentration was varied over fairly wide limits. If the hypobromous acid

[1] Cf. Bancroft: Jour. Phys. Chem., **13**, 20 (1909).
[2] Weisz: Zeit. phys. Chem., **54**, 351 (1906).
[3] Zeit. phys. Chem., **23**, 592 (1897).

were sufficiently dilute, it appeared to have very little effect one way or the other. When more concentrated, it enabled us to get a much better normal image than we should otherwise have obtained. In fact, it is an admirable agent for removing fog.

Further investigations showed that both of Abney's generalizations are inaccurate in the form in which they are usually put. It is not true that oxidizing agents facilitate the reversal; but it is true that one gets a better, reversed plate after development if oxidizing agents are present in the film during exposure. It is not true that depolarizers check the reversal; but it is true that they produce results which mask the reversal.

This discovery destroyed the foundations of the oxybromide theory and we are therefore forced to conclude that the latent normal image consists primarily of silver and bromine only.[1] Of the subhalide theories so-called, Trivelli's is the latest and the most complete. I cannot accept any theory which postulates two silver subhalides neither of which can be reduced by the developer while one of them has catalytic properties and the other has not. A further argument against Trivelli's theory is that he comes to grief over Abney's experiments. A theory which accounts equally well for facts and for alleged facts is not a safe guide. I shall, therefore, try to show that all the observed phenomena can be accounted for on the assumption that the latent image, whether normal or reversed, consists essentially of silver and halogen. While it is necessary to assign certain properties to some of the intermediate stages, it is neither necessary nor desirable to assume the existence of allotropic modifications.

When studying solarization, it has been customary to make different exposures and to develop for a given length of time. The resulting densities are then plotted as ordinates

[1] Of course in so far as the substance in the gelatine plate is colloidal, it will not be absolutely pure.

against the degree of exposure as abscissas. Quantitative data for such curves are to be found in the papers of Hurter and Driffield, Sterry, Mees and Sheppard, and others. A qualitative diagram by Trivelli has been reproduced in the preceding paper.[1] In Fig. 1, I give an imaginary sketch of what one would get if one were to point the camera at the sun. The degrees of exposure of that portion of the plate on which the image of the sun is focussed will always be greater than that of the rest of the plate and consequently will always be represented by a point further to the right on the curve OABS. If the degree of exposure of the sky is represented by the point H and that of the sun by the point L, we see that the sun will develop black against a relatively light background. If the degree of exposure of the sky is repre-

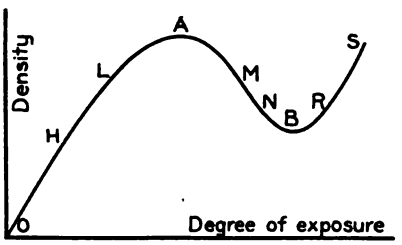

Fig. 1

sented by the point L and that of the sun by the point M, the developed plate will show the sun and the sky of the same degree of blackness and there will be no visible picture. If the two points are M and N, we shall get the sun coming out light against a relatively darker sky. In other words, we shall have a positive image instead of the negative which we got from H and L. If the degree of exposure of the sky be represented by R and that of the sun by S, we shall get a negative, the second negative as it is called. It has been pretty well established that this last image is due to the reduction of silver bromide to metallic silver by light. It is the image which we ordinarily get when we make prints with

[1] Jour. Phys. Chem., 13, 293 (1909).

albumenized paper. So far as the facts go, it seems probable that this metallic silver image is intensified when the plate is developed. This is a point which is apparently not of any especial importance so far as the theory of solarization is concerned.

The diagram shown in Fig. 1 is merely a qualitative graphical representation of observed facts. There is nothing in it to show the unknown degree of decomposition of the silver halide and yet that is what we need if we are going to account for the phenomena. I make two assumptions in regard to the behavior of the silver halides:

(1) The action of light on a silver halide corresponds to that of a direct current or of a fairly weak reducing agent. It causes the silver halide to pass through all the possible stages.

(2) A fairly strong reducing agent (a developer) does not cause the silver halide to pass through all the possible stages and does reduce certain silver-halogen solid solutions or subhalides faster than others which contain less halogen.

No one can take exception to the first assumption, which is merely a formal statement that the theory of Grotthuss applies to the case. It would be perfectly legitimate to object to the second assumption. It is avowedly an assumption *ad hoc*, and requires justification. Some day I hope to furnish experimental proof of this assumption; but that is not going to be an easy matter at best and may take a very long time. For the present, therefore, the usefulness of the assumption will have to be its justification. It is well, however, to note that the assumption is not an impossible one. We know that phenylhydroxylamine is ordinarily reduced to aniline without passing through the possible intermediate stages of azobenzene or hydrazobenzene. We also know that phenylhydroxylamine is reduced to aniline more rapidly than hydrazobenzene.

I agree entirely with Trivelli that a sharp distinction should be drawn between the ease or rate of development of a plate, and the sensitiveness of the plate to light. We

know that the rate of development of an unexposed plate is practically zero when an ordinary developer is used. When the silver bromide has lost a little bromine through exposure to light, the plate can be developed and therefore has a definite rate of development. On the other hand, the rate of development of metallic silver is of course zero. The rate of development for a given plate and a given developer, therefore, passes through a least one maximum as the composition of the silver salt changes from silver bromide to silver. The sensitiveness of the unexposed plate is high. Whether it is as high as that of a plate which has received an infinitesimal exposure is a point on which there is some difference of opinion; but which does not concern us at present. The important thing is that the rate of development may be low when the sensitiveness to light is high. This shows that the two sets of phenomena do not even run parallel.

In Fig. 2 are given exaggerated representations of the behavior of a plate with two different strengths of the same developer. The drawing is not to scale. The ordinates are rates of development while the variation of any grain of the emulsion between silver bromide and silver is represented along the abscissas. If the possible phases are a series of solid solutions from AgBr to Ag_2Br, and then the appearance of metallic silver, there will be a break in the curve at the composition Ag_2Br and metallic silver will be present beyond this point to an ever-increasing amount. It is not necessary, however, to assume any such state of things. So long as there is not a continuous series of solid solutions from silver bromide to silver, metallic silver will have to appear at some point before we reach the extreme right of the diagram and a break in the curve will occur wherever that point may be. If further investigation shows the existence of phases other than a solid solution and metallic silver, there will be breaks wherever the new phases appear.

If we postulate that the degree of reduction of the silver bromide is some direct function of the light intensity into the time of exposure, the abscissas also represent

degrees of exposure in unknown units. This is indicated by the words "degree of exposure" and by the symbols o and X. In so far as the blackening of the plate is proportional to the rate of development, we could measure densities along the ordinates as in Fig. 1. The curve for density and degree of exposure ceases to correspond to that for rate of development and composition at the point B in Fig. 1, where metallic silver first appears.

As in Fig. 1, for any given exposure, the high lights will be represented by points on the curves in Fig. 2 lying to the right of the corresponding points for the shadows. The curve OAB represents the action when a normal developer is used. At A, the maximum of the curve, we get the greatest blackening for a given time of development. If a plate is exposed for a short time, so that the decomposition in the high lights is represented by the point A or by some point

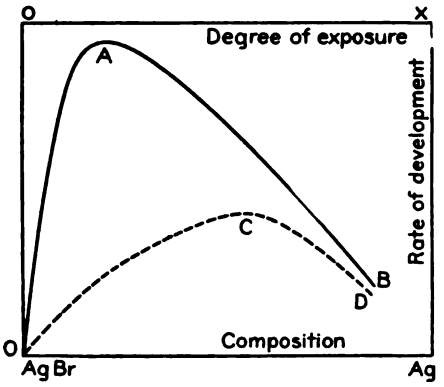

Fig. 2

to the left of that, the decomposition in the shadows will be represented by a point still nearer to O. The diagram shows that, in this case, the high lights will develop faster than the shadows, giving us a negative. If we expose for so long a time that the decomposition in the shadows corresponds to A or to some point to the right of it, the decomposition in the high lights will be represented by some point further down the curve towards B. The shadows will develop

faster than the lights and we shall have a positive, in other words, a reversal of the image. For intermediate exposures in which the shadows are represented by a point to the left of A and the high lights by a point to the right of A, we shall get a partial reversal, the high lights reversing the first and the shadows reversing the last. If the difference between the high lights and the shadows is not very great or if the curve OAB is very flat at the top, an exposure corresponding to A for the half lights will give a plate which is pretty uniformly fogged. All these phenomena are matters of record and they have also been checked in my laboratory.

All the experiments which will be referred to in this paper were made with Cramer's Lantern Slide Plates. Plates were exposed in a printing frame behind a given lantern slide for different lengths of time. The intensity of the light, the distance of the plate from the light and the nature and composition of the developer were kept constant. With an exposure of two seconds a good negative was obtained on development. With an exposure of five minutes, a good positive was obtained on development. With an exposure of two and one-half minutes, the plate developed very flat and only partially reversed, the deep shadows being the last to change,

One reason for supposing that the curve OAB may be very flat and relatively broad at the top is that amateurs often over-expose their plates badly and yet it is very seldom that they get beyond the stage of fog and into the stage of partial or complete reversal.

Since the form of the curve OAB in Fig. 2 depends on the nature of the developer, the position of A may vary. If we should add something to the developer which would make the curve OA more nearly vertical and which would thus move A over very close to the axis of ordinates, we should have a reversed image with a much shorter exposure than is necessary when using the ordinary developer. This is perhaps what happens with Waterhouse's thiocarbamide developer; but we have not yet tested his method experimen-

tally, so I cannot speak definitely with regard to this. Of course, the really important thing is to explain why thiocarbamide should displace the maximum to the left. I do not care to offer any hypothesis in regard to this now; but I feel certain that a knowledge of how thiocarbamide acts will help us in finding out why it acts as it does.

If we start with a dilute developer or with a developer to which we have added a good deal of bromide, the rate of development will be less and we shall, therefore, get a curve corresponding to OCD in Fig. 2. Since we can obtain a fair negative with such a developer from a plate which would fog badly with a normal developer, we know that we must still be on the ascending portion of OC when we have already reached the top of the curve OAB. In other words, the point C lies to the right of the point A. I do not know whether the curve OCD lies entirely inside of OAB or whether it crosses the latter somewhere in the right-hand portion of the diagram. Since the matter is of no importance so far as this paper is concerned, I have adopted provisionally the simpler of the two hypotheses, that OCD lies entirely inside of OAB.

The relative positions of A and C have been deduced from the experimental facts in regard to the development of negatives after ordinary exposures. No assumption has been made in regard to the development of positives. From the diagram, we see, however, that exposures corresponding to points on the abscissas between A and C will develop as positives if we use the normal developer and as negatives if we use a weak or a restrained developer. In other words, the reversal of the image is checked by the use of a weak developer or of a restrained developer. It was this fact which caused Precht[1] to believe that polarization is a phenomenon of development only. There is, however, still another conclusion to be drawn from the two curves in the diagram. For exposures corresponding to points to the right of C we shall get positives with either developer, pro-

[1] Cf. Jour. Phys. Chem., 13, 76 (1909).

vided we do not expose for such a time that we get the second reversal. This has been confirmed experimentally. With a certain exposure, the plates developed as positives with the normal developer and as negatives with a diluted developer. With a still longer exposure, positives were obtained with both developers.

We next took up the question of the effect of a depolarizer in the film during the exposure. If a plate be dipped into a solution of a depolarizer and then given a long exposure, no reversal is obtained and the conclusion is therefore drawn that depolarizers prevent the reversal. We shall modify this conclusion radically if we take into account Eder's work on the latent image. Eder[1] believes that an over-exposed film usually contains three images in varying relative amounts: a latent normal image, a latent reversed image and a normal silver image. If we expose a plate in contact with a depolarizing solution, we increase the rate of reduction and consequently the intensity of the silver image very much. After development, we may have a reversed image on the plate but we shall not see it if the normal silver image formed during the exposure is the more intense. The reversal will have taken place but it will have been masked. When describing some experiments with silver bromide collodion to which a silver nitrate solution had been added, Eder[2] says: "The traces of silver nitrate which cling to the silver bromide even after long washing with water, cause a very quick and dense blackening of the plate, so that the reversal is quite masked by it. A short treatment of such a plate with nitric acid (sp. gr. 1.20), after the exposure and before the development, changes the plate to such an extent that reversal can readily be detected when the exposure is one thousand times the induction limit."

This normal silver image, which can be destroyed by nitric acid, is the one which constitutes the second reversal and which gives rise to the portion BRS in Fig. 1. Any

[1] Zeit. wiss. Photographie, 3, 338 (1905).
[2] Cf. Jour. Phys. Chem., 13, 60 (1909).

state of things which intensifies this normal silver image will tend to prevent the first reversal from showing. The reason why it is difficult to obtain reversals with silver chloride dry plates[1] is that light reduces silver chloride readily to metallic silver. Consequently the normal silver image before development is apt to be so intense as to mask any reversal.

Now that we know why the depolarizer acts as it does, it is clear that the way to obtain a reversal is to shorten the exposure and not to lengthen it. Experiments were accordingly made with plates which had been dipped into a solution of potassium nitrite. When a relatively short exposure was made, the plates developed as positives; with longer exposures the plates developed as negatives. Intermediate exposures gave partial reversals. Since we are dealing with a second reversal, the conditions are exactly opposite to those previously considered and the high lights are the first to change from positive to negative while the shadows remain black up to the last minute.

Lüppo-Cramer did not succeed in getting a reversal when he had sodium nitrite in the film; but he worked under absolutely unknown conditions. He says[2] himself that he dipped dry plates for two minutes in a two percent solution of sodium nitrite and then dried them. There is nothing to show how he dried them and consequently we do not know at all what the concentration of the sodium nitrite really was or whether it was the same in any two plates. All we can be sure of is that the solution in the film contained more than two percent of sodium nitrite.

It is probable, as suggested by Trivelli, that the experiments of Waterhouse with stained plates are really experiments with films containing weak depolarizers. Reversals would, therefore, take place with shorter exposures than in the case of plates which had not been stained. We have not yet had time to take up this point experimentally and so

[1] Lüppo-Cramer: Photographische Probleme, 153 (1907).
[2] Cf. Jour. Phys. Chem., 13, 183 (1909).

I cannot be certain that other factors may not have to be considered.

If the presence of a depolarizer masks the reversal but does not prevent it, there is no reason to suppose that the presence of oxidizing agents in the film will really increase the tendency to reverse. A plate was bathed in a dilute permanganate solution and then exposed along with another plate from the same box which had not been so treated. The conditions of exposure and of development were as nearly identical as possible for the two plates. It was possible to find a time of exposure such that the permanganate plate gave a negative on development and the other plate a positive. This particular oxidizing agent, therefore, apparently checks reversal instead of helping it. I do not care to lay any stress on this point because, of course, there is some absorption of light by the permanganate and the effective exposure was therefore somewhat less than with the other plate. Since there would be a slight oxidation of the developer, the permanganate plate was possibly developed with a somewhat weaker developer than the other, which would decrease the tendency to reverse. These are trifles however. The important fact is that treatment with an oxidizing agent does not cut down the time of exposure necessary to produce a reversal when we expose to the same source of light and develop with the same initial developer. On the other hand, with a good liberal over-exposure, the permanganate plate gives us a much clearer reversed image than does the plate which has not been treated. This is really what Abney observed and what he meant when he said that oxidizing agents facilitate reversal. The explanation is a very simple one. When we use no oxidizing agent, the finished plate contains a more intense reversed image and a less intense normal silver image. What we see is the difference between the two. Since the presence of depolarizers in the film causes a more rapid reduction to silver, the presence of an oxidizing agent will retard this same reduction. Our finished plate will then contain less of the normal silver image and will

therefore give us a clearer reversed image. The masking of the reversal is decreased by the presence in the film, during exposure, of a substance which checks the reduction to silver by light.

If we expose a plate for such a length of time that we are still on the curve OA in Fig. 2, we get a negative on development. If we make a second exposure to white light of uniform intensity before development, we increase the decomposition over the whole plate and bring the plate into a state corresponding to some portion of the curve AB. On developing, we then get a reversed image. This accounts for what Trivelli calls the Sabatier polarization. It is, of course, possible to make the exposures in the reverse order. Whether the resulting positive will be as good of its kind as a good negative depends on a number of factors, which I prefer to discuss at some other time when I take up the whole question of developing positives from instantaneous exposures.

Trivelli[1] states that a second exposure to light is identical in effect with an exposure during development. It seems to me very probable that there are some quantitative differences. As far as the qualitative side of the phenomenon is concerned, the matter is quite simple. The light pushes the plate along while the development is going on. If the effect of the light is relatively intense, the image develops as a positive. If the effect of the developer is the more important, we get a negative. In one experiment three plates were exposed for fifteen seconds each, behind the same lantern slide at the same distance from the same source of light. The same developer was used in each case; but the first plate was developed at a distance of one meter from a Welsbach burner and came out a negative. The second plate was developed at a distance of fifteen centimeters from the same Welsbach and came out a positive. The third plate was developed at a distance of fifty centimeters from the Welsbach and came out partly positive and partly negative.

[1] Zeit. wiss. Photographie, 6, 238 (1908).

There was one thing about the last plate which was distinctly interesting though it has nothing to do with the theory of solarization. We were copying a lantern slide made from a photograph of a distinguished French physicist dressed in his academic robes. The gown was black silk and there were large white buttons down the front. For obvious reasons it was impossible to see the shadows which the buttons cast upon the black gown. On the plate in question, everything had reversed except the gown and consequently we had the white buttons casting a black shadow on the apparently white gown.

We have now to consider the antagonistic effect of different lights, a phenomenon which Trivelli has called the Herschel effect. In the case of the silver halides, the matter is complicated by the formation of photo-halides having different colors and consequently absorbing light in different degrees. These are mere matters of detail and the general theory is quite simple. If we work with a sufficient quantity of pure silver halide in a closed space, there will be an equilibrium pressure of the halogen corresponding to the chemical potential of each wave-length of light or to the chemical potential of any other form of energy, cathode rays for instance, which tends to set free the halogen. If we pass from light which causes one equilibrium pressure to light which causes another equilibrium pressure, we shall have a change in the dissociation and consequently an antagonistic effect which may or may not lead to a reversal, depending on the conditions of the experiment. This appears very nicely in some experiments that Goldstein[1] made with a silver bromide so prepared that it was not sensitive to light. This salt is blackened by cathode rays and brought back to the yellow state by positive light of a certain intensity. Since positive light of a certain intensity blackens the salt, it was possible first to blacken and then to bleach it by changing the intensity of the positive light. Cathode rays set free

[1] Cf. Jour. Phys. Chem., 13, 48 (1909).

enough iodine from silver iodide to blacken the salt, positive light enough to stain it orange, while daylight restores the original color. Alkali salts can be colored by cathode rays or by ultra-violet light and are blackened by daylight. Goldstein also showed that, in a closed tube lighted from above, it is impossible to blacken both the upper and the under sides of the silver bromide simultaneously. What is at the moment the surface is always blackened while the under side loses its black color.

"With a continuous illumination in the open air, diffusion and air currents prevent the utilization of the free bromine and there is, therefore, an increasing blackening and decomposition without regeneration."

This question of diffusion is probably of extreme importance in several cases. If the grain of the silver bromide gelatine plate is relatively coarse, some of the bromine set free by light will gather in the inner portion of the grain and will tend to prevent the reduction to silver. With such plates, we should expect to get a reversed image without difficulty and this is exactly what happens. With a fine-grained emulsion there is a greater tendency for the bromine to pass off and an increased tendency for the reduction to silver to take place. Lüppo-Cramer[1] states that it is impossible to obtain reversal phenomena with a silver bromide gelatine having an extraordinarily fine grain. I think it is much more probable that this is a case of masked reversal and I am inclined to offer the same explanation in regard to the difficulty of obtaining reversals with pure silver bromide containing no binder.

In the Clayden effect, a very short exposure to an intense light followed by brief exposure to diffused light causes a reversal while no reversal is obtained if the original exposure is longer than about one fifty-thousandth of a second. The fact of the reversal presents no difficulty at all. We know that the more intense the primary exposure, the less intense

[1] Photographische Probleme, 147 (1907).

does the secondary exposure have to be in order to cause a reversal. The troublesome fact is that no reversal takes place if the original exposure is prolonged beyond a very brief interval. We have not yet had time to repeat these experiments and consequently I cannot be certain as to the explanation. I suspect, however, that we are dealing with a case of masked reversal. Abney worked with a light of moderate intensity and added a depolarizer to the film. Clayden worked with a light of great intensity and added no depolarizer to the film. In the experiment previously referred to, Eder showed that a reversal did take place in the case of silver bromide collodion to which silver nitrate had been added, and I hope to be able to show the same thing some day for the Clayden effect.

Trivelli[1] has called attention to a case in which an Eastman film was developed three years after exposure and came out a positive instead of a negative. In the last few months my attention has been called by Prof. Moler of Cornell, by Prof. Friedburg of the College of the City of New York, and by others to cases in which films had developed as positives instead of negatives. In every case an interval of several months or more had elapsed between the exposure and the development. The explanation offered by Trivelli is undoubtedly the right one, that chemical decompositions in the film had produced the same effect as a longer exposure to light. In the film shown me by Professor Moler, apparently the whole picture had reversed except where the sunlight fell on the white collar of a man. That half of the collar was black. At first sight this seems abnormal because we usually have the high lights reversing before the shadows. It all becomes intelligible if we assume that the chemical reduction due to, or accompanying, the decomposition of the film has carried the plate along nearly to the point where we get the second reversal and the appearance of the normal silver image. When discussing the effect of a reducing agent

[1] Cf. Jour. Phys. Chem., 13, 309 (1909).

in the film, I have pointed out that the change from positive to negative takes place first in the high lights. I therefore conclude that the blackness of the man's collar was due to a second reversal and not to the first reversal having failed to take place. A necessary corollary is that by treatment with certain chemicals one ought to be able to bring a plate from the point where it will develop as a negative to a point where it will develop as a positive or even to a point where we get a second negative. This apparently was done by Carey Lea[1] twenty years ago, using sodium hypophosphite as the preliminary reducing agent.

The theory outlined in this paper is a very simple one involving practically no assumptions. It is based on the theory of Grotthuss and appears to be a logical deduction from the experimental fact that silver bromide which has been slightly decomposed by light is reduced faster by a developer than either silver bromide which has not been exposed at all or silver bromide which has been completely decomposed by light. The theory seems able to account for all the phenomena of reversal and it reconciles the divergent views of such men as Abney, Eder, Lüppo-Cramer, Englisch, and Precht. In the next paper I expect to discuss the methods of developing a positive after an instantaneous exposure. There are also some points in regard to the experiments of Nipher, Luggin and others which can perfectly well be left till later.

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[1] Am. Jour. Sci. (3), **33**, 486 (1887)

ON THE REFRACTIVE INDICES OF SOLUTIONS OF THE CASEINATES AND THE ACID- AND ALKALI-EQUIVALENTS OF CASEIN

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I. Introduction

In carrying out experiments of a physico-chemical character upon proteins, we are continually hampered by our lack of any method of determining quantities and concentrations of proteins with any approach to exactitude. Direct gravimetric methods either involve great loss of material in the process of freeing the protein thoroughly from water, or else are rendered grossly inaccurate through the uncertain hydration of the protein material which is weighed. Volumetric methods which involve titrations are subject, where solutions containing proteins are concerned, to numerous errors of unusual magnitude, arising from a variety of causes. In the first place, the high molecular weights of the proteins lead to a relatively large mass of protein being equivalent to relatively small volumes of the solutions employed in titration, so that the errors arising from the estimation of these volumes are correspondingly high. Then, again, we absolutely lack in most cases that knowledge of the quantitative equivalence between a given protein and some other substance which we must possess before any titration can be sucessfully employed. Even where we do possess a knowledge of this equivalence, as in the case of casein, we possess no certainty that the equivalent measured represents the formation of a definite chemical compound, so that our estimation of the equivalent usually depends upon the change in color of some arbitrarily chosen indicator, while, owing to the amphoteric character of the proteins it is usually impossible to obtain, in their presence, sharp changes in the color of

indicators. Indirect methods of estimation such as that of determining the nitrogen by the Kjeldahl method and dividing the figure obtained by the percentage of nitrogen in the protein are tedious and subject to numerous inaccuracies.

In the case of casein, thanks to the labors of Söldner,[1] Courant,[2] de Jager,[3] Timpe,[4] Kobrak,[5] Laqueur and Sackur,[6] and Van Slyke and Hart,[7] we do possess, as I have said, a knowledge of the equivalent between casein and the alkalies and alkaline earths at neutrality to a given indicator, phenolphthalein, and upon this the author based a volumetric method of determining the percentage of casein in solutions which is fairly rapid and, comparatively speaking, accurate,[8] nevertheless the determinations made by this method are subject to errors of 5% or more.

All these facts strongly suggest that the ordinary chemical methods of estimation cannot be successfully employed where proteins are concerned, and that we must resort to methods depending primarily upon the measurement of *physical* qualities of their solutions. The large size of the protein molecule, which is a drawback when chemical methods of estimation are employed, may, in many cases where physical measurements are in question, be a positive advantage. This is particularly the case where the quantity measured is one, such as the refractive index, which depends upon the *size* of the molecule, being greater the greater the molecular volume. Hence, although the refractive index of their solutions cannot, as a rule, be successfully employed in the quantitative determination of small concentrations of inorganic

[1] Söldner Landw. Versuchsstat., **35**, 351 (1888).

[2] Courant. Arch. ges. Physiol., **50**, 109 (1891).

[3] L. de Jager, Nederl. Tijdschr. v. Geneesk., **2**, 253 (1897), quoted from Jahresber. f. Thierchem., **27**, 276 (1897).

[4] H. Timpe, Arch. f. Hyg., **18**, 1 (1893), quoted after Raudnitz, Ergeb. d. Physiol., **2**, 193 (1903).

[5] E. Kobrak, Arch. f. d. ges. Physiol., **80**, 69 (1900).

[6] Laqueur and Sackur Beitr. z. Chem. Physiol. u. Path., **3**, 193 (1902).

[7] Van Slyke and Hart, Am. Chem. Jour., **33**, 461 (1905).

[8] T. Brailsford Robertson, Jour. Biol. Chem., **2**, 317 (1907).

substances in water, yet there are grounds for hoping that it may be successfully employed for the estimation of the concentration of solutions of substances of high molecular volume such as the proteins.

Accordingly, and with this hope, the following investigations were undertaken.

II. Experimental

The casein employed in these experiments was the C. P. product manufactured by Eimer and Amend and further purified by trituration with large volumes of distilled water, alcohol (absolute) and ether (u. n. d.); it was dried for 24 hours at 36°. The properties of the product thus obtained have been fully described by me in a previous paper;[1] it gives every indication of being a pure product, being insoluble in distilled water (save in traces which adhere to the undissolved particles) and completely precipitated by acetic acid. It neutralizes to phenolphthalein exactly the quantity of base determined by Laqueur and Sackur and by Van Slyke and Hart.[2] It is free from appreciable water, but is associated with a small quantity of ether, the last traces of which are somewhat difficult to drive off.

Accurately weighed quantities of this product were dissolved each in 100 cc. of solutions of NaOH of various concentrations.[3] The refractive indices of the solutions were determined by means of a Pulfrich Refractometer.[4] In this way it was found that, in the first place, dissolved caseinates change the refractive index of water to a far greater degree than do ordinary inorganic salts in equivalent-molecular concentration and, in the second place, that in a given concentration of alkali *the difference between the refractive indices of two solutions is proportional to the difference between the*

[1] T. Brailsford Robertson, l. c.

[2] Laqueur and Sackur, l. c. Van Slyke and Hart, l. c.

[3] In order to ensure complete solution, the mixtures were stirred rapidly and continuously for an hour at room temperature. In the case of the more concentrated solutions, the stirring was continued for a longer period.

[4] Very kindly lent to me by the Department of Chemistry.

percentages of casein which they contain. This fact can be expressed algebraically as follows:

$$n - n_1 = a \times c$$

where n is the observed refractive index of the solution, c is the percentage of casein which it contains and n_1 and a are constants.

The following tables summarize the results thus obtained. In the first column of each table is given the amount of casein in grams which was dissolved in 100 cc. of the solution. In the second column is given the refractive index of the solution measured at 20° C. In the third column is given the value of the constant a calculated from the above formula for the given value of the constant n_1. The constant n_1 is determined in the following manner: the differences between the refractive indices of successive solutions differing equally in casein-content are averaged and this average is subtracted from the refractive index of the solution differing from the solution containing no casein by the same casein-content. Thus, in Table II (solvent N/50 NaOH) differences in refractive index corresponding to successive increments in casein-concentration of 0.5 percent are, respectively, 0.0008, 0.0007, 0.0008, 0.0007, and the average of these is 0.00076; subtracting this from the refractive index of the solution containing 0.5 percent of casein, we obtain $n_1 = 1.33364$. In the fourth column is given the concentration of casein *calculated* from the above formula, for the value of n_1 determined in the manner just described and for the average value of a. At the head of each table is given the concentration of alkali in which the casein was dissolved.

TABLE I

Solvent 0.01 *N* NaOH

Concentration of Casein percent	Refractive index	a for n_1 = 1.33332	Concentration of casein (calculated) percent
0.25	1.3337	0.00152	0.253
0.50	1.3341	0.00156	0.520
0.75	1.3344	0.00144	0.720
1.00	1.3348	0.00148	0.987
1.25	1.3352	0.00150	1.253
1.50	1.3356	0.00152	1.520
		average, 0.00150	

TABLE II

Solvent 0.02 *N* NaOH

Concentration of casein percent	Refractive index	a for n_1 = 1.33364	Concentration of casein (calculated) percent
0.5	1.3344	0.00152	0.49
1.0	1.3352	0.00156	1.00
1.5	1.3360	0.00157	1.52
2.0	1.3367	0.00153	1.97
2.5	1.3375	0.00154	2.49
3.0	1.3382	0.00152	2.94
		average, 0.00155	

TABLE III

Solvent 0.03 *N* NaOH

Concentration of casein percent	Refractive index	a for n_1 = 1.33364	Concentration of casein (calculated) percent
0.5	1.3344	0.00152	0.49
1.0	1.3351	0.00146	0.94
1.5	1.3360	0.00157	1.52
2.0	1.3368	0.00158	2.04
2.5	1.3376	0.00158	2.55
3.0	1.3382	0.00152	2.94
		average, 0.00155	

TABLE IV

Solvent 0.05 *N* NaOH

Concentration of casein percent	Refractive index	a for $n_1 = 1.33396$	Concentration of casein (calculated) percent
0.5	1.3347	0.00148	0.51
1.0	1.3354	0.00144	0.99
1.5	1.3362	0.00149	1.54
2.0	1.3370	0.00152	2.08
2.5	1.3376	0.00146	2.49
3.0	1.3384	0.00148	3.04
		average, 0.00146	

TABLE V

Solvent 0.10 *N* NaOH

Concentration casein percent	Refractive index	a for $n_1 = 1.33444$	Concentration of casein (calculated) percent
0.5	1.3352	0.00152	0.50
1.0	1.3360	0.00156	1.02
1.5	1.3368	0.00157	1.54
2.0	1.3375	0.00153	2.00
2.5	1.3383	0.00154	2.52
3.0	1.3390	0.00152	2.98
4.0	1.3405	0.00152	3.96
5.0	1.3420	0.00151	4.94
6.0	1.3436	0.00153	5.99
		average, 0.00153	

It is at once evident that, in the first place, the formula

$$n - n_1 = a \times c$$

is very accurately obeyed and, in the second place, that these experiments have justified our anticipation that it would be possible to measure the concentration of protein solutions much more accurately by their refractive indices than by chemical methods, for the agreement between the actual and the calculated concentrations of casein is extremely close, far closer than that obtained by methods of estimation

which involve titrations. The Pulfrich Refractometer reads to within 1′, and 1′ of the angle of total reflection roughly corresponds to a change of 0.0001 in the refractive index, which is therefore the possible error of the determination; since a change of 0.0015 in the refractive index corresponds to a change of 1 gram in the casein-content of 100 cc., the possible error in the determination of 1 gram of casein in 100 cc. by this method is 1/15th, *i. e.*, 7 percent, the possible error for more dilute solutions being proportionately greater, for more concentrated solutions proportionately less. A glance at the Tables I-V will serve to show that the actual error of the determinations is in all cases less than the possible error and usually considerably less, seldom amounting to more than 2 percent.

The value of a is sufficiently constant throughout the series to justify the statement that it is independent of the concentration of the alkali in which the casein is dissolved; its average value for all the determinations is 0.00152. Some of these solutions were acid to phenolphthalein and others were alkaline; now I have pointed out elsewhere[1] that in solutions acid to phenolphthalein the casein is probably polymerized, possessing in these solutions a higher molecular weight than in solutions neutral or alkaline to phenolphthalein. In other words, *no matter in what manner the casein is combined with the base, the change in the refractive index of a given volume of a solution of a base which is brought about by the introduction of a given weight of casein is constant; if the volume be 100 cc and the weight of casein 1 gram, the change in the refractive index is 0.00152.*

The value of the constant n_1 is obviously dependent upon the concentration of the base, being the refractive index of the solution of the base in which no casein is dissolved; the change in hydroxyl concentration consequent upon the addition of casein to these solutions is, apparently,

[1] T. Brailsford Robertson, Jour. Phys. Chem., **10**, 524 (1906); **11**, 453 (1907); **12**, 473 (1908); Jour. Biol. Chem., **4**, 23 (1908). T. Brailsford Robertson and Theo. C. Burnett, Jour. Biol. Chem., **6**, 105 (1909).

in all cases insufficient to appreciably affect their refractive indices although, of course, it is very appreciable to indicators. It was thought better to determine the value of n_1 by interpolation as described above than to determine it directly, since the method of interpolation enables us to determine it with greater precision. The refractive index of N/10 NaOH was, however, determined directly and found to be 1.3344 at 20° C, a value in as good agreement with the value 1.33444 determined by interpolation (cf. Table V.) as the accuracy of the direct determination permits. The equation $n - n_1 = a \times c$ holds good, not only for solutions of casein in solutions of NaOH, but also for solutions of casein in other solvents; this is shown by the following results, in which the solution employed to dissolve the casein was N/20 NH_4OH:

TABLE VI

Solvent 0.05 *N* NH_4OH

Concentration of casein percent	Refractive index	a for n_1 = 1.33364	Concentration of casein (calculated) percent
1.0	1.3351	0.00156	0.99
2.0	1.3368	0.00163	2.06
3.0	1.3383	0.00159	3.01
4.0	1.3399	0.00159	4.04
6.0	1.3428	0.00154	5.86
		average, 0.00158	

In dilute solutions of bases, the differences between the values of n_1 for the different bases are negligible. If 2.5 grams of casein be dissolved in 100 cc each of 0.02 *N* solutions of NaOH, LiOH, NH_4OH, $Sr(OH)_2$, $Ba(OH)_2$ and $Ca(OH)_2$ the refractive indices of the solutions are in every case identical, namely, 1.3375. *Hence the value of a, that is, of the change in refractive index which is brought about by the addition of 1 gram of casein to 100 cc of a solution of a base is independent of the nature of the base.* Moreover, the value of a is the same in acid as in alkaline solutions. Thus

the refractive index of a 1.25 percent solution of casein in 0.01 *N* NaOH is 1.3352, and of a 1.25 percent solution of casein in 0.01 *N* NaCl + 0.00513 *N* HCl is also 1.3352. Hence, *whether the casein is acting as an acid or as a base, its effect upon the refractive index of the solution to which it is added is quantitatively the same.*

The Influence of Temperature upon the Refractive Indices of Solutions of the Caseinates

Since the refractive index of fluids varies, as a rule, notably with temperature, it becomes of importance, if the refractive index of casein solutions is to be used as a measure of their concentration, to determine in what manner the refractive indices of solutions of the caseinates is dependent upon the temperature, since it would be inconvenient always to determine the refractive index at a fixed standard temperature. Moreover, the investigation of the change in refractive index, which these solutions undergo between the temperatures of 30° and 40°, is of considerable theoretical interest, since a marked increase in the opalescence, conductivity and alkalinity of casein solutions occurs at a temperature in the neighborhood of 36°.[1] It has been suggested by W. A. Osborne that this phenomenon is attributable to an increase in the hydrolytic dissociation of the caseinates at this temperature, the insoluble casein thus set free being held in suspension; while I have elsewhere pointed out that the facts are equally readily explained by supposing that the casein undergoes polymerization as the temperature rises, with consequent diminution in its alkali-binding power.[2] Two and a half grams of casein were dissolved in 100 cc of NaOH. Some of the solution was placed in the refractometer and surrounded with the jacket supplied with the instrument for maintaining the prism and the solution at a given temperature. The temperature was then slowly raised by running hot water through the jacket; a thermometer was placed

[1] W. A. Osborne, Jour. Physiol., **27**, 398 (1901).
[2] T. Brailsford Robertson, Jour. Biol. Chem., **5**, 147 (1908).

in the solution and the temperature and the angle of total reflection were read at intervals; the readings were repeated as the solution cooled; both sets of readings are given in Table VII, those which were taken while the solution was *cooling* being distinguished by an asterisk.

Solutions of the caseinates of the alkaline earths and lithium undergo a marked increase in opalescence as the temperature approaches 36°. The caseinates of sodium, potassium and ammonium do not undergo an increase in opalescence at this temperature which is appreciable to the unaided eye, but that they do undergo a slight increase in opalescence is revealed by the fact that the edge of the shadow which marks the angle of total reflection becomes somewhat indistinct and furry as the temperature rises to between 30° and 40°; hence the experimental error and the difficulty of the determination are somewhat increased at these temperatures.

In the accompanying table, the temperature at which the determination was made is given in the first column, in the second is given the refractive index of the solution at that temperature, and in the third, the difference between the refractive index of the solution and that of water at the same temperature. The refractive index of water at the various temperatures indicated, is estimated by interpolation from the determinations of Rühlmann, quoted in Landolt-Börnstein's Physikalisch-Chemische Taballen, 0.0001 being subtracted from the refractive index of water for every 1° C rise in temperature between 20° and 30° and 0.00013 for every degree rise in temperature between 30° and 40°, the refractive index at 20° being taken as 1.3330.

It will be observed that there is no sudden alteration in the refractive index of this solution between the temperatures 30° and 40°, on the contrary, the difference between the refractive index of the solution and that of water at the same temperature remains appreciably constant. In other words, *the change in refractive index which is brought about by the addition of a given quantity of casein to a given*

TABLE VII

2.5 grams of Casein dissolved in 100 cc of 0.02 *N* NaOH

Temperature	Refractive index of solution	Difference between refractive index of solution and that of water at the same temperature
20°	1.3375	0.0045
25°	1.3371	0.0046
* 25.5°	1.3370	0.00455
* 26°	1.3369	0.0045
28°	1.3366	0.0044
* 28.5°	1.3365	0.00435
30°	1.3364	0.0044
* 32°	1.3361	0.0044
32.5°	1.3362	0.0045
* 33.5°	1.3360	0.00445
34°	1.3360	0.0045
* 35°	1.3358	0.00445
* 36°	1.3354	0.0042
38.5°	1.3351	0.0042
* 38.5°	1.3353	0.0044
40°	1.3350	0.0043
* 40°	1.3351	0.0044
		average, 0.0044

volume of an alkaline solution is, within the limits of experimental error and between the temperatures 20° C and 40° C, constant. This fact speaks in favor rather of the author's hypothesis regarding the changes in solutions of the caseinates with rising temperature than of Osborne's hypothesis. Were insoluble casein set free and suspended in the solution at a temperature lying between 30° and 40°, we should expect a sudden drop in the refractive index of the solution at this temperature; no such drop is observed. If, on the contrary, the effect of rise of temperature were merely to cause polymerization of the casein molecule, then since, as we have seen, the change in refractive index which is brought about by the addition of casein to an alkaline solution is independent of the manner in which the casein is combined with the base, no sudden change in refractive index would be expected with rise of temperature, on the con-

trary, the observed constancy of the difference between the refractive index of the solution and that of water at the same temperature would rather be expected, since the percentage of casein actually in solution would be the same at all temperatures.

No irreversible change in the refractive index of casein solutions is brought about by heating even to higher temperatures than 40° (unless soluble inorganic salts of the alkaline earths be present, *vide infra*) and there is no appreciable "residual effect" on cooling. Solutions of the caseinates can be rapidly heated to boiling and as rapidly cooled without changing their refractive indices.[1]

The Acid-equivalent of Casein

Advantage was taken of the marked change in refractive index which accompanies change in the casein-content of solutions to determine the acid-equivalent of casein, *i. e.*, the maximum amount of casein which a given amount of acid will hold in solution. Here an interesting phenomenon is encountered; if one stirs excess of casein in 0.1 *N* HCl (or more dilute) rapidly and continuously for over an hour very little or no casein goes into solution, the solution remains perfectly clear on filtration and its refractive index is only very slightly changed. If, however, the casein be previously dissolved in dilute NaOH and then precipitated with HCl, the addition of even slight excess of HCl will then carry it into solution. In other words, dry, granular casein only dissolves with extreme slowness in acid solutions,[2] while wet, flocculent and freshly precipitated casein dissolves readily

[1] This also shows that the trace of ether associated with the preparation employed in these experiments has no appreciable influence upon the refractive indices of the solutions.

[2] Van Slyke and Van Slyke, Am. Chem. Jour., **38**, 393 (1907); Jour. Biol. Chem., **4**, 259 (1908), have shown that dry casein, while insoluble in dilute acids, abstracts acid from the solution; they consider that the acid is "adsorbed" or concentrated by capillary forces at the surface of the casein particles. I have elsewhere, Jour. Biol. Chem., **4**, 35 (1908); Zeit. Chemie und Industrie der Kolloide, **3**, 18 (1908), dwelt upon the objections to this view.

in excess of acid. This effect is not due to the presence of a trace of salt, such as NaCl, in the latter case, because the addition of 0.01 *N* NaCl to a 0.1 *N* HCl solution does not, to any appreciable extent, enhance the rapidity with which casein dissolves in the solution. The same phenomenon is encountered in the case of serum globulin (the fraction insoluble in distilled water, precipitable by CO_2) and has been repeatedly remarked upon by investigators. Serum globulin which is wet and has never been dried since precipitation, readily and rapidly dissolves in alkaline solutions, while the dried powder dissolves comparatively slowly.

The acid equivalent of casein was determined in the following manner: 2.5 grams of casein were dissolved in 100 cc of 0.02 *N* NaOH and to the solutions thus obtained varying quantities of 0.1 *N* HCl, made up to 100 cc with distilled water, were added, and the resulting mixtures were stirred rapidly for from 1/2 to 1 hour; they were then filtered and the refractive indices of the filtrates were determined. Since the refractive indices of mixtures in the same proportion and concentrations of NaOH and HCl differ only inappreciably from one another, a constant refractive index (= 1.3352, cf. Table I) indicated complete solution of the casein.

In the following tables, the excess of acid (over that required to neutralize the NaOH) is given in the first column, and in the second is given the refractive index of the filtered solution. Since the concentration of Na in all the solutions is 0.01, we may, with sufficient approach to accuracy, write down the casein-content of the solutions from those of solutions of the same refractive index in Table I of this paper; this has been done in column 3. In the fourth column is given the ratio of the excess of acid to the concentration of the dissolved casein.

TABLE VIII

Excess of acid	Refractive index	Concentration of casein	Ratio of excess of HCl to concentration of casein
0.002100 *N*	1.3341	0.52	0.00404
0.002705 *N*	1.3344	0.72	0.00376
0.003310 *N*	1.3348	0.99	0.00334
0.003915 *N*	1.3351	1.19	0.00330
0.004520 *N*	1.3352	1.25	—
0.005125 *N*	1.3352	1.25	—

TABLE IX

Excess of acid	Refractive index	Concentration of casein percent	Ratio of excess of HCl to concentration of casein
0.002100 *N*	1.3340	0.45	0.0047
0.003610 *N*	1.3349	1.05	0.0034
0.005125 *N*	1.3352	1.25	—
0.008150 *N*	1.3352	1.25	—
0.01420 *N*	1.3352	1.25	—
0.02025 *N*	1.3352	1.25	—

The ratios in the fourth column are approximately constant, that is, the increment in casein-concentration is, within the limits of experimental error, very nearly proportional to the excess of HCl in the solution,[1] hence, averaging the increments in casein-concentration for equal increments in HCl-excess we can readily, by interpolation, determine the excess of HCl which was *just* sufficient to completely dissolve one gram of casein; in each of the experiments tabulated above this is found to be 0.00164 *N*. Since 200 cc of 0.00164 *N* HCl = 3.28 cc of N/10 HCl, one cc of N/10 HCl = 0.305 gram of casein, or, in other words, *1 gram of casein = 32.8 × 10^{-5} equivalent-gram-molecules of HCl.*

The above determinations must be regarded as being

[1] There are, however, indications that the acid-equivalent is higher the more dilute the solution; the same phenomenon is encountered, but to a more marked degree, in acid solutions of Serum Globulin; cf. W. B. Hardy, Jour. Physiol., **33**, 266 (1905).

somewhat approximate, since a small amount of NaCl is present in the solution and we do not know whether, or to what extent, salts enhance or depress the solubility of casein in acids. The influence of the salt upon the acid-equivalent cannot, however, be very great, since, if it were so, it might be expected to vary with the nature of the salt, and the equivalent in the presence of NH_4Cl is, within the limits of experimental error, the same as that in the presence of NaCl. This is shown by the following table. The determinations were made in precisely the same manner as those described above, save that N/50 NH_4OH was employed to dissolve the casein instead of N/50 NaOH.

TABLE X

Excess of acid	Refractive index	Concentration of casein percent	Ratio of excess of HCl to concentration of casein
0.002100 *N*	1.3341	0.52	0.0040
0.003610 *N*	1.3350	1.12	0.0032
0.005125 *N*	1.3352	1.25	—

By interpolation we find that the excess of acid which was just sufficient to dissolve 1 gram of casein was 0.00158 *N*, *i. e.*, 1 gram of casein = 31.6×10^{-5} equivalent-gram-molecules of HCl, which is, within the limits of experimental error, identical with the figure previously obtained. The acid-equivalent of casein is thus much higher than that of serum globulin.[1]

The Alkali-equivalent of Casein

In a previous paper I have stated that the maximum amount of casein which an alkaline solution will dissolve is that with which the amount of base present will combine to form "neutral" caseinate, neutral to litmus, containing an amount of the base equivalent to 1.57 percent of CaO.[2] Using the more sensitive and exact method of determining

[1] Cf. W. B. Hardy, l. c.

[2] T. Brailsford Robertson, Jour. Biol. Chem., 2, 317 (1907).

the concentration of casein in solution which is described above, however, I was not long in discovering that this statement is erroneous and that casein is far more soluble in alkalies than previous estimates would lead us to suppose.

The source of error lies in the fact that complete "saturation" of an alkaline solution with casein is almost impossible to obtain by shaking the solution with excess of casein. The solutions which I considered "saturated" in my previous publication were, in reality, very far from containing all the casein which the base would dissolve because, after the attainment of neutrality to litmus, additional casein dissolves only with extreme slowness. Even prior to the attainment of neutrality to litmus, however, the process of solution occupies a definite and considerable period of time, and rapidity of solution is less in solutions of strong bases than in solutions of strong bases. This is very clearly shown by the following table. Six grams of casein were stirred rapidly and continuously in 100 cc of the alkali mentioned in the first column, for the time given in the second column. The refractive indices of the filtered solutions are given in the second column, and the estimated casein-contents, calculated from the refractive indices, are given in the fourth column.

TABLE XI

Solvent	Stirred for	Refractive index	Concentration of casein (calculated)
0.02 *N* NaOH	1 hour	1.3425	5.7
0.02 *N* LiOH	1 "	1.3426	5.8
0.02 *N* NH_4OH	1 "	1.3411	4.8
0.02 *N* NH_4OH	2½ "	1.3420	5.4
0.02 *N* NH_4OH	4½ "	1.3426	5.8
0.02 *N* $Sr(OH)_2$	2 "	1.3398	4.0
0.02 *N* $Ca(OH)_2$	2 "	1.3382	3.0
0.02 *N* $Ba(OH)_2$	2 "	1.3374	2.4

It is evident that this solution of the casein takes place rapidly at first, very slowly later on, and that the strong bases dissolve casein much more rapidly than weak bases.

Even six hours of stirring with a large excess of casein failed to secure a complete saturation of the alkali. Hence the following procedure was adopted: 4 grams of casein were dissolved in 100 cc of N/40 NaOH and varying amounts of N/10 HCl, made up to 100 cc with distilled water were added, so as to leave varying excesses of NaOH unneutralized by HCl. The excess of alkali which was *just* sufficient to completely dissolve the casein (indicated by a constant refractive index of 1.3367 of the filtered solution) was then determined and found to be 4.55 cc of 0.1 *N* NaOH. In other words 1 cc of N/10 NaOH = 0.877 gram of casein at "saturation," or 1 gram of casein = 11.4×10^{-5} equivalent-gram-molecules of NaOH, an equivalent of the same order as the alkali equivalent, at "saturation," of serum-globulin.[1] The equivalent for LiOH is identical with that for NaOH.

The alkali-equivalents for $Sr(OH)_2$, $Ba(OH)_2$ and $Ca(OH)_2$ cannot be determined in this manner because the chloride of the alkaline earth completely precipitates the caseinate which is formed.[2] That this effect is an instance of the well-known phenomenon of "precipitation by a common ion" is shown by the following phenomenon. If to 100 cc of N/50 $Ca(OH)_2$, containing 2.5 grams of casein, we add 100 cc of N/50 $CaCl_2$ no actual precipitation occurs, it is true, but a marked increase in its opalescence is observed. If, however, we add, instead of N/50 $CaCl_2$, N/50 $SrCl_2$, no change in the opacity of the solution occurs; yet if $SrCl_2$ be added to a solution of casein in $Sr(OH)_2$ the caseinate is precipitated just as readily and completely as that in solution in $Ca(OH)_2$ is precipitated by $CaCl_2$. Of course, if sufficient *excess* of a chloride of an alkaline earth be added to a solution of casein in a dilute hydroxide of another alkaline earth, the casein will be precipitated, since, in that case, a sufficient quantity of the caseinate of the first alkaline earth is formed,

[1] W. B. Hardy, l. c.

[2] Cf. T. Brailsford Robertson, l. c.

by double decomposition, to undergo precipitation by the excess of the chloride.[1]

The fully "saturated" solutions of the caseinates obtained by the method outlined above are, of course, acid to litmus, since in solutions neutral to litmus 1 gram of casein = 53×10^{-5} equivalent-gram-molecules of the base,[2] while in the "saturated" solutions 1 gram of casein = 11.4×10^{-5} equivalent-gram-molecules of the base. The acidity of these solutions is, however, surprisingly disproportionate to the emphatic difference between the alkali-equivalents of the casein in saturated and in neutral solutions. The reactions of the "saturated" solutions to indicators are as follows:

Dimethylaminoazobenzol	Yellow
Congo red	Red
[3]Sodium alizarinsulphonate	Red
Cochineal	Rose
Paranitrophenol	Colorless
Rosolic acid	Yellow

indicating a H^+ concentration of between 10^{-5} and 10^{-6} N and a hydroxyl concentration of between 10^{-9} and 10^{-8} N.[4]

[1] It is of interest to note that the casein is precipitated in flocculi from both of these solutions by heating to boiling and that this precipitate does not redissolve on cooling. The same phenomenon, save that it occurs at a lower temperature, was observed by Sidney Ringer, in solutions of paracasein (cf. S. Ringer, Jour. Physiol., **12**, 164 (1891), also Ringer and Sainsbury, Ibid., **11**, 369 (1890); **12**, 170 (1891)). In the absence of soluble inorganic salts of the alkaline earths, of course, no precipitation occurs on heating, and the increase in opalescence which occurs at 36° disappears on cooling.

[2] Van Slyke and Hart: Am. Chem. Jour., **33**, 470 (1905).

[3] It is possible by means of this indicator, to demonstrate in a very striking manner, the amphoteric character of casein. If to a solution of casein in dilute NaOH, and containing sufficient alizarinsulphonate of sodium to render it bright red, one adds sufficient HCl to precipitate and *partially* redissolve the casein, on stirring and allowing the undissolved casein to settle, it can be seen that the supernatant, acid fluid is dark brown, while the precipitate is stained bright *pink*, or, in other words, that, when suspended in an *acid* solution, casein is acting as a base. All the indicators used were Gruebler's preparations, being the same as those employed by Salm, *vide infra*.

[4] E. Salm: Zeit. phys. Chem., **57**, 471 (1907).

In other words, although in passing from the "saturated" to the "neutral" caseinate the amount of alkali bound by 1 gram of casein changes by 40×10^{-5} gram-equivalents, yet the hydroxyl-content of a solution containing 1 gram of casein only changes by 10^{-7} or 1/4000th of the change in the concentration of the base. Even in passing from the "saturated" to the "basic" caseinate (neutral to phenolphthalein, 1 gram of casein = 80×10^{-5} equivalent-gram-molecules of alkali, cf. Van Slyke and Hart, l. c.), the change in hydroxyl-concentration of a solution containing 1 gram of casein is still only about 1/350th of the change in the concentration of the base. Hence the caseinates possess in a very high degree the power of maintaining the neutrality of solutions in which they occur. I have elsewhere suggested[1] that this phenomenon is to be attributed to the amphoteric-acid structure of the protein molecule and the power of almost undergoing indefinite polymerization[2] which this structure confers upon them.

III. Conclusions

(1) The difference between the refractive indices of two solutions of a caseinate which differ only in their casein-content, is proportional to the difference between the percentages of casein which they contain. This relation can be expressed algebraically as follows:

$$n - n_1 = a \times c$$

where n is the observed refractive index of the solution, c is the percentage of casein which it contains, n_1 is a constant the value of which depends upon the concentration and nature of the solvent employed to dissolve the casein, and a is a constant numerically equal to the change in the refractive index of the solvent which is brought about by the addition to 100 cc of 1 gram of casein.

[1] T. Brailsford Robertson: Jour. Phys. Chem., **10**, 524 (1906); **11**, 453 (1907); **12**, 473 (1908); Jour. Biol. Chem., **4**, 23 (1908); **5**, 147 (1908). T. Brailsford Robertson and Theo. C. Burnett: Jour. Biol. Chem., **6**, 105 (1909).

[2] Or, more accurately, *condensation* with the elimination of the elements of water.

(2) By means of the above formula the concentration of casein in a solution can be very accurately determined, the deviations from accuracy rarely exceeding 2 percent of the quantity of casein contained in 100 cc of the solution.

(3) The change in the refractive index of a given volume of a solution of a base which is brought about by the introduction of a given weight of casein is independent of the concentration of the base and of the nature of the base; if the volume be 100 cc and the weight of casein 1 gram, the change in the refractive index is 0.00152.

(4) The change in the refractive index of a given volume of a solution which is brought about by the introduction of a given weight of casein is the same in solutions of HCl as in solutions of the bases; hence, whether the casein is acting as an acid or as a base, its effect upon the refractive index of the solution to which it is added is quantitatively the same.

(5) The difference between the refractive index of a solution of sodium caseinate and that of water at the same temperature is independent of the temperature between 20° and 40°; hence the change in refractive index which is brought about by the addition of casein to a given volume of an alkaline solution is, between 20° and 40°, constant.

(6) The hydrochloric-acid-equivalent of casein (*i. e.*, the ntity of acid required to just dissolve 1 gram of casein) has been determined, by methods described in this paper, and, for solutions containing 1.25 percent of casein, it was found that 1 gram of casein = approx. 32×10^{-5} equivalent-gram-molecules of HCl.

(7) Casein dissolves in alkaline solutions, at first rapidly and later more slowly. After the attainment of neutrality to litmus, additional casein dissolves only with extreme slowness. For this reason the author's previous statement that the maximum amount of casein which an alkaline solution will dissolve is that with which the amount of base present will combine to form the "neutral" caseinate (neutral to litmus) is erroneous.

(8) The NaOH-equivalent of casein has been determined, by methods described in this paper, for solutions containing 2 percent of casein, and it was found that 1 gram of casein, at "saturation" of the base = 11.4×10^{-5} equivalent-gram-molecules of NaOH. The LiOH-equivalent was found to be identical with the NaOH-equivalent.

(9) The acidity of solutions of bases "saturated" with casein was determined by means of indicators and was found to lie between 10^{-5} and 10^{-6} N H^+; the hydroxyl-concentration in these solutions, therefore, lies between 10^{-9} and 10^{-8} *N*.

CRYSTALLIZATION THROUGH MEMBRANES

BY JAMES H. WALTON, JR.

In his "Studien über die Bildung und Umwandlung fester Körper" Ostwald[1] has shown that upon adding very minute fragments of the solid phase to a super-saturated solution or an under-cooled liquid crystallization takes place immediately.

Carefully performed experiments with super-saturated solutions of sodium chlorate, sodium potassium tartrate, barium chloride, borax, potassium alum and under-cooled salol, thymol, and sodium thiosulphate showed that there is a limit to the size of the crystal which will induce crystallization. This limit is very low, in the case of salol a crystal of 10^{-7} gram causes the under-cooled liquid to crystallize while a crystal of 10^{-8} gram causes no formation of crystals.

While reviewing Ostwald's work it occurred to the author to make the following experiment. Divide a supersaturated solution into two parts by means of filter paper, and by introducing a crystal into one part allow crystallization to take place. The object of this experiment was to see whether or not the crystals which form in the pores of the filter paper are of sufficient size to cause crystallization to take place in the other part of the solution.

To test this idea experiments were carried out with a supersaturated solution of sodium sulphate. This solution was of such a concentration that when crystallization took place the whole mass became solidified. A number of tubes were made by cutting off the closed end of an ordinary five-inch test tube. Over the flanged end of the tubes were tied various kinds of filter paper—ordinary qualitative, quantitative and hardened. In this and in subsequent experiments care was taken to have the filter paper extend at least an inch from the flanged end of the tube. The paper was tied securely by means of strong linen thread. The tubes were

[1] Zeit. phys. Chem., **22**, 289 (1897).

then placed in a beaker containing the supersaturated solution, the lower end of the tube standing about a quarter of an inch below the surface of the liquid. Since the filter paper extended about an inch above the surface of the liquid in the beaker, danger of leakage taking place between the paper and the glass was prevented.

Experiment 1.—A few cubic centimeters of the supersaturated liquid were poured into the tube and after standing a few minutes a crystal of sodium sulphate was placed in the tube. Crystallization took place and in each case crystals formed in the beaker, starting from the lower side of the paper, thus showing conclusively that the crystallization had been transmitted through the filter paper.

Since the crystallization took place through the filter paper with such ease, experiments were made in which this substance was replaced by some of the membranes which are ordinarily used in dialysis. For this purpose ordinary parchment paper, collodion and gold beaters' skin were used. The parchment paper was the ordinary grade supplied by dealers. The collodion films were prepared according to the method described by Bigelow.[1] A solution of collodion was poured upon a surface of mercury which was about five inches in diameter. When the film was sufficiently hard to be removed it was placed in distilled water and preserved for the experiment. In some of the experiments performed the membranes had been prepared but twenty minutes, in others they were several days old. The results obtained, however, were the same. The gold beaters' skin was very thin, and was of the grade supplied by dealers in chemical apparatus.

In these experiments great difficulty was experienced in preventing premature crystallization of the supersaturated solutions. This is especially true after one has worked with the same substance for two or three days. The air becomes filled with the crystal dust to such an extent that a super-

[1] Jour. Am. Chem. Soc., 29, 1675 (1907)

saturated solution can be preserved in an open vessel for only a very few minutes. The spreading of dust will be prevented in a large measure if care is taken after working with the solutions, not to rub the hands on a towel but to wash them thoroughly in running water. Pipettes and similar apparatus used in working with the aqueous solutions should be kept in a dish of water to prevent evaporation of liquid which may have been left on the surface with subsequent spreading of dust. The solutions are best prepared and preserved in ordinary 250 cc. flasks, the necks of which have been sealed by drawing them out in a flame. This permits the outside of the flask to be washed free from any dust. To remove the solution it is best to take the flask into a different room from that in which the solution was prepared, open it by breaking off the sealed tip and remove the liquid by means of a pipette. The flask is best closed by means of a cap made of absorbent cotton.

The method of procedure in these experiments was as follows: The supersaturated solution was placed in a test-tube about four inches long, and the membrane tied securely over the mouth of the tube. In the case of undercooled liquids a few crystals were placed in the tube, they were melted and the tube closed with the membrane. The tube was then inverted and allowed to rest upon the bottom of a small beaker containing enough of the supersaturated solution to fill it to the depth of about one quarter of an inch. After standing for a few minutes the liquid in the beaker was inoculated with a crystal.

Experiment 2.—A supersaturated solution of sodium sulphate was used, the following results being obtained.:

Gold beaters' skin. Crystallization took place in the tube in less than one minute after the solution in the beaker was inoculated.

Parchment paper. Crystallization in the tube in about one minute.

Collodion. In several experiments the length of time necessary for crystallization varied from 15 to 30 minutes.

In order to see whether or not the phenomenon noted in this experiment is specific, or whether the crystals of other supersaturated solutions can be transmitted through membranes, the following experiments were tried:

Experiment 3.—A supersaturated solution of borax was prepared and an experiment similar to the above was carried out, using the same kinds of membranes. The results obtained were similar to those of Experiment 2, the times necessary for the appearance of crystals inside the tubes being as follows:

Gold beaters' skin	3 minutes
Collodion	10 "
Parchment	10 "

Experiment 4.—At high temperatures sodium acetate is very soluble in water and upon cooling forms a supersaturated solution. Upon making experiments similar to the foregoing, using this salt, it was found that the transmission of crystals occurred with the three different membranes in less than one minute after the liquids in the beakers had been inoculated. Besides the three membranes mentioned above, a rubber membrane of approximately 0.005 inch thickness, similar to that employed by Kahlenberg[1] in his experiments on osmosis, was also used with a supersaturated solution of sodium acetate. No crystals separated on the inside of the tube, even after it had stood for several days, the outside of the rubber being in contact with sodium acetate crystals during the whole time.

The transmission of crystals through rubber was further tested by using a supersaturated solution of potassium alum, this substance, as was shown by Ostwald, being extremely sensitive to the slightest trace of the solid phase. In fact it is so sensitive that the preparation of a supersaturated solution was more difficult than any other solution used in these experiments. This was accomplished by preparing a

[1] Jour. Phys. Chem., 10, 141 (1906).

saturated solution in a flask, heating it to boiling and filtering it into a test tube. The tube was then closed with the rubber membrane, and the hot liquid moved back and forth to dissolve any particles which might adhere to the side of the tube. A solution prepared in this way was tested as in the case of the experiments with sodium acetate and the rubber membrane. It stood for several days without crystallizing. Further experiments with the rubber membrane were made as follows: A supersaturated solution was placed in a strong glass distilling flask of about 200 cc capacity, and a piece of rubber tied firmly over the mouth of the flask. A piece of rubber tube provided with a strong pinch clamp was placed over the side arm of the flask. By blowing into the flask the rubber over the neck could be blown out into a spherical form and on closing the clamp the rubber remained distended. From the normal thickness of the rubber and the diameter of the mouth of the flask it was possible to calculate the thickness of the expanded rubber. This was found to be 0.0003–0.0004 inch. The flask was inverted so that the supersaturated solution could run down inside the rubber balloon and crystallization started on the outside of the balloon.

Using a supersaturated solution of sodium acetate the following results were observed in eight experiments:

In five cases crystals appeared to be transmitted through the membrane, the time varying from ten minutes to twelve hours. In the other cases crystallization did not occur. In one case undercooled sodium acetate prepared by melting the salt in its crystal water was used instead of the supersaturated solution, and stood for six days under conditions similar to the foregoing without crystallization taking place. In this experiment, as in some of the others it was noticed that if the rubber was pressed even very gently the crystals began to separate from the solution at once.

In two experiments with supersaturated potassium alum solutions crystallization also appeared to be transmitted through the rubber, the time in one case being about thirty minutes, in the other the crystals separating during the night.

In the above experiments with the thin membranes the rubber was stretched to the point just short of disruption.

Several of the rubber membranes through which the crystallization had been transmitted were tested for holes by blowing them out and placing on one side a solution of ferric chloride, on the other potassium sulphocyanate solution. No coloration of the sulphocyanate occurred, even after standing for several hours. Similarly some of the membranes were tested with a solution of potassium iodide on one side and water on the other. The water was tested for iodine by acidifying, adding hydrogen peroxide, then starch solution. Here, as in the previous case, negative results were obtained.

Experiment 6.—A supersaturated solution of sodium thiosulphate was used, the results obtained being similar to those with the borax and sodium sulphate, only in this case it took longer for the crystals to appear inside the tube, as is shown below.

Parchment.....	20 minutes
Collodion.....	15 " to 2 hours in different experiments
Gold beaters' skin..	1 minute

Experiment 7.—With the exception of the alum, the salts used in the foregoing experiments were those of sodium. It was of interest to see whether or not the salts of heavier metals would show a difference of behavior. Lead acetate easily forms a supersaturated solution and was used for this purpose. With the gold beaters' skin the results were similar to those already obtained. In the case of the parchment and also the collodion several hours elapsed before crystals separated on the inside of the tube. It was noticed that the length of time of transmission increased considerably with the thickness of the collodion. It seemed probable that this was due to the fact that the collodion and parchment were saturated with water, and before the crystallization could occur in the tube it was necessary to replace this water with

the supersaturated solution. This idea was tested as follows: Tubes covered with collodion membranes and containing supersaturated solutions of lead acetate were allowed to stand in beakers of supersaturated solution for fifteen hours, so that the membrane would have an opportunity to become thoroughly saturated with the solution. At the end of that time the solution in the beakers was inoculated and inside of three minutes crystals appeared in the tubes. The extreme length of time necessary for transmission of the crystals was therefore due primarily to the slowness of diffusion of the lead acetate.

Undercooled Liquids

A large number of substances, particularly organic compounds, easily form undercooled liquids. It was interesting to see if their behavior towards membranes was similar to the supersaturated solutions.

Experiment 8.—Water was cooled to —4° by placing it in a small U-tube arranged as shown in the figure.

This was made by cutting off one arm of the U-tube, placing a membrane over the short arm and slipping over the membrane a piece of tube with diameter slightly larger than that of the U-tube. The first experiment was made with gold beaters' skin. The tube was placed in the bath and after its contents had cooled to the temperature of the surrounding liquid a fragment of ice was introduced into the tube at A. The liquid crystallized at once, and in less than one minute crystals appeared in the lower part of the U-tube, spreading from the bottom of the membrane in the direction of the arrow. The results were confirmed by repeating the experiment. Similar results were obtained when collodion was used. In five experiments the time in which the crystals appeared on the lower side of the collodion membrane varied from two to five minutes.

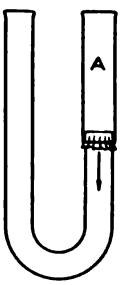

Fig. 1

The experiments were repeated using a rubber membrane but no crystallization took place in the lower tube.

Experiment 9.—Thymol was melted and then allowed to become undercooled. A number of experiments were made with this substance, the method used being exactly the same as in the experiments with sodium acetate. The membranes used were collodion, which had been allowed to dry without wetting, gold beaters' skin and rubber. In each case the crystallization was transmitted through the membrane, although the time necessary varied considerably with the different membranes.

Rubber	15–30 minutes
Collodion	1¼ hours
Gold beaters' skin	10 minutes

The rubber membrane was removed after the experiment and washed with alcohol. Upon examination it was found to be intact.

An undercooled solution of salol gave similar results with rubber, the crystals appearing in twelve minutes.

Acetophenone was used in addition to the above undercooled liquids, the time necessary for the appearance of crystals being as follows:

Collodion	2 minutes
Rubber	37 "

Experiment 10.—Phenol melts at approximately 43°, but may be undercooled to about 24°, at which temperature it solidifies.[1]

The range of temperatures through which the undercooling may take place may be widened by adding a little water to the phenol. To about 5 cc of the liquid phenol a few drops of water were added and experiments made with parchment and rubber membranes. With the parchment

[1] Moore: Zeit. phys. Chem., 12, 545 (1893).

the crystals appeared in the tube in seven minutes, with the rubber no separation of crystals took place. In several experiments which were carried out with the rubber membranes the liquid in the tube remained unchanged for several days. As soon as the rubber was removed and crystals added the separation of crystals occurred, showing that the solution was still undercooled.

This experiment was repeated, a few drops of benzene being added to the liquid phenol instead of the water. Crystals formed in the tube, the time in several experiments varying from two to seven minutes.

Experiment 11.—Frog's skin and the membrane which surrounds an egg were used with a supersaturated solution of sodium sulphate, the experiments being carried out similarly to those already described.

The skin was removed from the frog and the experiment made within seven minutes from the time the frog was killed. The results were similar to those obtained when sodium sulphate and gold beaters' skin were used. It made no difference whether the crystallization was started from the inside or the outside of the frog skin, the transmission of crystals appeared to take place equally well in either direction.

The white and yolk of an egg were carefully removed, leaving the lower part of the membrane unbroken. A small portion of the shell was removed from the bottom of the egg. The egg was then filled with a supersaturated sodium sulphate solution and placed in a beaker containing some of the same solution. In different experiments crystallization was started in the egg and in the beaker respectively. In each case, however, the crystals appeared almost instantaneously on the opposite side of the membrane, showing that the crystals are transmitted equally well in either direction.

Summary and Conclusions

The results obtained in these experiments are collected in the following tables:

TABLE 1

Supersaturated solutions

	Parchment	Collodion	Gold beaters' skin	Rubber 0.005 inches thick
Sodium sulphate....	1 min.[1]	15–30 min.	1 min.	—
Sodium acetate.....	1 min.	1 min.	1 min.	no
Borax.....	10 min.	10 min.	3 min.	—
Sodium thiosulphate	20 min.	15 m.–2 hrs.	1 min.	—
Potassium alum.....	—	—	—	no
Lead acetate.....	1–3 hrs.	3 m.–14 hrs.	1 min.	—

TABLE 2

Undercooled liquids

	Parchment	Collodion	Gold beaters' skin	Rubber 0.005 inches thick
Water.....	—	2–5 min.	1 min.	no
Thymol.....	—	75 min.	10 min.	15–30 min.
Salol.....	—	—	—	12 min.
Acetophenone.....	—	2 min.	—	37 min.
Phenol + water.....	7 min.	—	—	no
Phenol + benzene..	—	—	—	2–7 min.

With the supersaturated aqueous solution it will be seen that wherever water alone can pass through the membrane it is also possible for crystallization to be transmitted.

With the expanded rubber an apparent exception to this general rule has been found, but here it must be remembered that the membrane is under abnormal conditions, being subjected to a strain just short of the amount necessary to cause its disruption. Under these conditions the possibility of a crystal being mechanically forced through the membrane would appear far from remote. It would seem as if such a mechanical action would leave an opening which, for the time being, might be closed by a crystal. By washing, however, the crystal would be dissolved and a solution like ferric

[1] Time necessary in each case for transmission of crystals through the respective membranes.

chloride or potassium iodide should be able to pass through this opening. It has already been shown that this is not the case. No definite conclusions as to the behavior of these extremely thin membranes can be made at this time, the whole matter will be made the subject of further investigation.

In the case of the undercooled organic liquids it is seen that crystallization takes place *via* the rubber membrane. These are all liquids which are similar in nature to rubber, they consequently would be expected to saturate the rubber and permit the transmission of crystallization in a manner analogous to the saturation and transmission of parchment or collodion by sodium acetate solution. This is also substantiated by the results obtained with phenol. A small amount of water added to the phenol prevents the saturation of the rubber membrane and consequently the transmission of the crystallization. If the water is replaced by benzene, however, the transmission occurs as with the salol and thymol.

University of Wisconsin

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Electricity, Sound, and Light. *By Robert Andrews Millikan and John Mills. 14 × 21 cm; pp. iv + 389. Boston: Ginn & Co. Price: $2.00; mailing price, $2.15.*—"This book represents primarily an attempt to secure a satisfactory articulation of the laboratory and class-room phases of instruction in physics. It is an outgrowth of the conviction that in courses of intermediate grade in colleges, universities, and engineering schools a real insight into the methods of physics, and a thorough grasp of its foundation principles are not readily gained unless theory is presented in immediate connection with such concrete laboratory problems as are calculated to give the student a sound basis for intelligent theoretical work.

"Nevertheless the book is intended to be much more than a laboratory manual. It represents an attempt to present a complete logical development, from the standpoint of theory as well as experiment, of the subjects indicated in the title."

The headings of the chapters are: magnetic and electric fields of force; determination of the strengths of magnetic fields and magnetic poles; measurements of electric currents; measurement of potential differences; measurement of resistance; temperature coefficient of resistance; galvanometer constant of a moving-coil galvanometer; absolute measurement of capacity; comparison of capacities, determination of dielectric constants, and the ratio of the electrostatic and electro-magnetic units; electromotive force and internal resistance; comparison of electromotive forces; electro-magnetic induction; constants of the earth's magnetic field; self-induction; magnetic induction in iron; electrolytic conduction; velocity of sound in air; musical properties of air chambers; longitudinal vibration of rods; waves in strings; diffraction of sound and light waves; diffraction grating; refraction of light; total reflection; photometry; dispersion and spectra; polarized light; radioactivity.

This seems to be a very useful book and one to be recommended to the chemist. The chapter on radioactivity is unusually clear. On p. 181, however, the authors credit to Clausius a good deal larger share of the electrolytic dissociation theory than really belongs to him. Clausius never postulated any quantitative relation between molecular conductivity and dissociation. In fact, Clausius never assumed anything more than an infinitesimal dissociation under any circumstances. *Wilder D. Bancroft*

Physikalische Chemie der Metalle. *Sechs Vorträge über die wissenschaftlichen Grundlagen der Metallurgie. By Rudolf Schenck. 18 × 26 cm; pp. iv + 193. Halle: Wilhelm Knapp, 1909. Price: paper, 7.00 marks; bound, 7.50 marks.*—The volume is the outgrowth of a course of lectures delivered in 1907 before the engineers of the Rhine provinces. The subject was treated under six heads: general properties of the metals; metallic solutions and alloys; alloys of the metals with carbides; oxygen and sulphides; metallurgical reactions; decomposition of carbon monoxide; blast furnace reactions; the reactions of the sulphides.

The author is unfortunate in that he wrote his book just before Upton's paper on the carbon-steels appeared. The result is that this portion of the book was obsolete before it appeared. The rest of the book is interesting though there is some question whether the physical chemistry here presented is really of much use to technical men. One cannot help feeling that there is a certain lack of contact. *Wilder D. Bancroft*

Grundriss der allgemeinen Chemie. *By Wilhelm Ostwald. Vierte, völlig umgearbeitete Aüflage. 16 × 24 cm; pp. ix + 661. Leipzig: Wilhelm Engelmann, 1909. Price: linen, 21.20 marks; bound, 22.50 marks.*—This new edition differs from the preceding ones in two respects. The phase rule point of view is predominant throughout and there is a very marked epistemological tendency. To one who knows the subject already, the book is more interesting than ever, because it goes deeper. It will not, however, arouse the enthusiasm in the beginner, which so many of us felt in regard to the first edition.

Concurrently with the change in the point of view there has come a lack of interest in regard to details. Many statements re-appear in this edition even though their inaccuracy is a matter about which there can no longer be any dispute. On p. 113, we have the familiar law that what is in equilibrium in one way is in equilibrium in all ways. Saturated solutions of salt in alcohol and in water are in equilibrium with the same solid phase; but they are not in equilibrium with each other. On p. 334, we read that catalytic agents do not displace the equilibrium. This is not true for a solvent and it is not true for what are apparently irreversible reactions. On p. 460, we have the erroneous statement that two solutions which are isohydric with a third solution are necessarily isohydric with each other. The color of methyl orange as an indicator, p. 474, is referred to the sulphonic acid group, although we get practically the same color changes when there is no sulphonic group present.

The voltage of the gas cell is given on p. 509, as 1.06 volts and no one could tell from the text that the surface tension method does not give true single potential differences. On p. 521, the excess voltage for mercury is stated to be due largely to the smoothness of the liquid surface in spite of the fact that frozen mercury shows the same characteristics.

The reviewer admits frankly that he cannot understand the point of view which makes it possible for a man to put in Fig. 36 on p. 356 and still to maintain that the only difference between solvent and solute is one of relative masses. Some day the present attitude of the chemical world in regard to this point, will be looked upon as analogous to that of the fetich worshipper.

The last three sections of the book deal with microchemistry, photochemistry, and chemical affinity. When we have a two-phase system in which one phase occurs as a number of separated masses while the other phase forms a continuous mass, the first is called the dispersed phase and the second the dispersing phase or medium. When there are only two phases to be considered, they may be classified as follows:

(*a*) The dispersing phase is gaseous. Since two gas phases cannot coexist, the second phase must be either liquid or solid. If liquid, we are dealing with a fog; if solid, with a dust.

(*b*) The dispersing phase is liquid. Gas bubbles in a liquid form foam; liquids in a liquid form a milk; and solids in a liquid form slimes.

(*c*) The dispersing phase is solid. Gas bubbles create a pumice-like structure. Liquids give rise to the entrapped drops so familiar to the mineralogists, while solids give solid mixtures. Pulverulent mixtures of solids do not belong under this head because powders are really solid particles in air or, in other words, dust.

So far as one can judge, Ostwald accepts the Brownian movements, p. 542, at their face value. Of course, that is the most natural and obvious thing to do; but the reviewer has always had a sneaking feeling that the particles only danced when some one was looking. The fact that particles have been seen to dance to-day and also ten years ago is no proof that they have been vibrating continuously during those years. The question is whether the particles vibrate because they are in an inhomogeneous field or because it is their nature to. We know that they will march and countermarch under the influence of an electric current, we know that they are electrically charged, and we know that they are in an inhomogeneous field all the time that we watch them; but we do not know as yet whether the actual motion is due entirely to the inhomogeneity of the field or not. Ostwald looks upon the calculations of Einstein and of Smoluchowski as final, in view of the experiments of Svedberg; but an elaborate mathematical calculation is a thing to be tested very carefully.

Wilder D. Bancroft

General Chemistry for Colleges. *By Alexander Smith. 13 × 21 cm; pp. xiii + 529. New York: The Century Co., 1908.*—"The present work differs from the Author's Introduction to General Inorganic Chemistry, in being intended for pupils who can devote less time to the study of the science, and whose needs can be satisfied by a less extensive course. It resembles the larger work in the arrangement of the contents and in the general method of treatment. The matter, and particularly the theoretical matter, however, has been simplified and has been confined strictly to the most fundamental topics. Such parts of the theory, as are thus given, are presented with the same fullness as before, and are illustrated and applied with all the persistence needed to insure full apprehension and, ultimately, spontaneous employment by the student. Such parts as could not be treated in this way, within the limits set by the plan of the book, have been omitted."

One of the problems confronting every teacher of elementary chemistry is as to the amount of physical chemistry to be introduced into such a course. The answer to the problem depends largely on the amount of physical chemistry which the teacher happens to know. Consequently, we are not surprised to find a lot of it in this book.

In the chapter on solution, the subheads are: general properties of solutions; the scope of the word; limits of solubility; recognition and measurement of solubility; terminology; solution, one of the physical states of aggregation of matter; kinetic-molecular hypothesis applied to the state of solution; kinetic-molecular hypothesis applied to the process of solution; independent solubility; two immiscible solvents and law of partition; influence of temperature on solubility; equilibrium in a saturated solution.

In the chapter on chemical equilibrium, the subheads are: reversible actions; kinetic explanation; chemical equilibrium and its characteristics; the influence of temperature; the influence of concentration; formulation of the law of molecular concentration; the forward action in homogeneous and inhomogeneous systems; the reverse action and displacement of equilibrium.

In the chapter on dissociation, the subheads are: some characteristic properties of acids, bases, and salts, shown in aqueous solution; freezing-points of solutions; laws of freezing-point depression; freezing-points and dissociation in solution; the constitution of solutions of acids, bases, and salts.

In the chapter on ionization, the subheads are: introductory; non-electrolytes; chemical changes taking place at the electrodes during electrolysis; ionic migration; the hypothesis of ions; application to the explanation of electrolysis; difficulties presented by this hypothesis; résumé and nomenclature; ionic equilibrium; applications to the interpretation of conductivity measurements; constitution of solutions of ionogens; relation of ionization to chemical activity.

In the chapter on ionic substances and their interaction, the subheads are: mixed ionogens and double salts; the kinds of ionic substances furnished by ionogens; ionic equilibrium with a single ionogen; displacement of ionic equilibria; double decomposition in solution; precipitation; neutralization; acidimetry and alkalimetry; indicators; displacement and the electromotive series; non-ionic modes of forming ionogens.

Scattered through the other chapters are such things as the solubility product, precipitation by a common ion, increase of solubility when a complex salt is formed, etc., etc. From all this it is easy to see that the enthusiastic freshman is expected to learn a good deal of physical chemistry. Whether he can digest so much so early in his chemical studies is a matter to be decided experimentally. Presumably, it depends very much on the teacher.

On p. 410, there is an objectionable phrase where the author speaks of "a current of less than 0.5 volt." The reviewer feels also that a more sparing use of the kinetic hypothesis would be advantageous; but this is a matter of taste. In most respects, the book is an admirable one, concise and clear.

Wilder D. Bancroft

Exercises in Elementary Quantitative Chemical Analysis. *For Students of Agriculture. By Azariah Thomas Lincoln and James Henri Walton. 15 × 22 cm; pp. xiii + 218. New York: The Macmillan Company, 1907. Price: $1.50 net.*—"Owing to the growing demand for quantitative analytical chemistry by those engaged in the study of agriculture, it seemed to the authors that the presentation of the fundamental methods of agricultural analysis as carried out in the laboratories of the American Experiment Stations would be desirable. While this book is designed primarily as an elementary quantitative guide for the use of agricultural students, it may also be used for the work in general elementary quantitative analysis."

The book is divided into five sections: introduction; gravimetric analysis; volumetric analysis; agricultural analysis; stoichiometry. Under agricultural analysis, are given methods for analyzing milk, butter, cereals and feeding materials, fertilizers, and soils. The directions are clear, and the book should prove serviceable to those for whom it is written. *Wilder D. Bancroft*

THE SPECIFIC GRAVITY AND PERCENTAGE STRENGTH OF SELENIC ACID

BY M. E. DIEMER AND VICTOR LENHER

It has been very desirable in making certain studies with selenic acid to have the density and percentage strength data for various concentrations of the pure acid. The only available table is that prepared by Cameron and Macallen[1] in their studies on selenic acid.

The observations which they have made have been corroborated by us, and are excellent for the range of concentration through which they worked. Their figures are from 99.73 percent to 73.43. For acid more dilute than 73.43 percent, no data are available. We have therefore deemed it advisable to study the more dilute solutions, as well as the stronger acid.

Preparation of Selenic Acid

The starting material was fused stick selenium bought on the open market. This selenium was powdered, and treated with nitric acid diluted with an equal quantity of water. The resulting solution was evaporated to dryness to expel the nitric acid, the selenium dioxide taken up in water and the insoluble matter always found in commercial selenium filtered off. The sulphur was removed by adding barium hydroxide to the dilute aqueous solution of the dioxide until further addition failed to produce a permanent precipitate. The barium sulphate was removed by filtration, and the solution evaporated to dryness. The dioxide was resublimed until white.

Two methods for the preparation of the selenic acid from this dioxide were used. In the first method diluted silver nitrate solution was treated with a dilute solution of selenium dioxide in water, and the resulting insoluble silver selenite washed free from all soluble compounds. The silver selenite

[1] Chem. News, 59, 259 (1889).

was suspended in water and treated with bromine water, when silver bromide and selenic acid were produced. The dilute selenic acid after filtration from the silver bromide, was concentrated by boiling under diminished pressure. A pressure of 30 mm and a temperature of 100 degrees completely removes the excess of bromine and any nitric acid. The final traces of selenous acid were removed by dilution and treatment with hydrogen sulphide. After filtering off the small amount of selenium precipitated, the excess of hydrogen sulphide was removed and the acid concentrated by heating under diminished pressure. The final concentration was made at a temperature of 185° and a pressure of 10 mm, solid potassium hydroxide being placed in the condenser to facilitate the dehydration. Careful tests of this acid after dilution showed it to be free from sulphuric and selenous acids.

A second preparation of the acid was made by fusing the purified selenium dioxide with potassium nitrate and obtaining potassium selenate. To a dilute solution of the fusion lead nitrate was added, insoluble lead selenate being formed. This precipitate was thoroughly washed with water after which it was suspended in water and treated with hydrogen sulphide. The lead sulphide obtained was removed by filtration, and the resulting dilute solution concentrated under diminished pressure as in the first preparation. The resulting acid proved to be free, as shown by careful tests, from sulphuric and selenous acids.

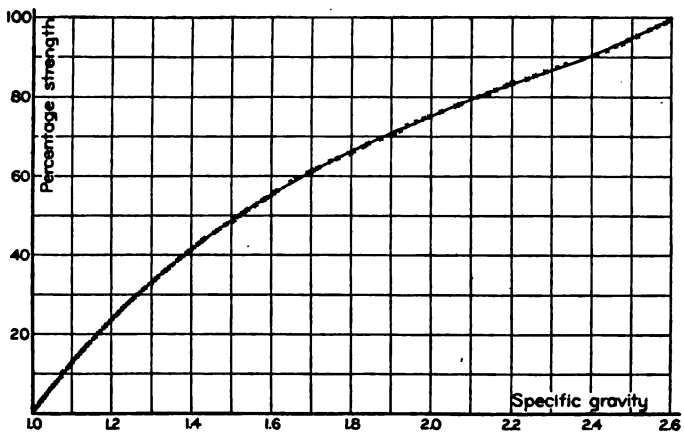
The purity of the acids was also ascertained by evaporation on platinum foil and subsequent ignition, no residue was found in any case, showing absence of nonvolatile impurities.

The water used in making the dilutions for the weaker acids was distilled three times, once from alkali and once from acid.

The acid was introduced into a Sprengel pycnometer and the latter placed in a thermostat whose temperature was maintained at 20° to within one-tenth of a degree, by a temperature control. It was measured at this temperature

after which the pycnometer containing the acid was weighed at room temperature.

The weights used were carefully adjusted in connection with this work, and the weighings given are corrected to 4° and vacuum. The specific gravities given are in the liquid state at 20° referred to the density of water at 4°.



The strength of the acid was determined by transferring a portion from the pycnometer and reweighing. After dilution with the appropriate amount of water it was titrated with a tenth normal solution of sodium carbonate, using methyl orange as the indicator. The sodium carbonate solution was prepared from repeatedly crystallized and ignited sodium bicarbonate, and was compared with a standard solution of sulphuric acid whose content had been determined gravimetrically. In the determination of the strength of the selenic acid, appropriate weights were taken so that the error of titration should not exceed 0.08 percent of the selenic acid content.

All of the determinations have been made in duplicate.

Results by determination. $\frac{20^\circ}{4^\circ}$ Vacuum

Specific gravity	Percent	Specific gravity	Percent	Specific gravity	Percent
1.0048	0.89	1.3138	34.25	1.8405	68.08
1.0083	1.33	1.3300	35.72	1.8716	69.37
1.0177	2.58	1.3404	36.45	1.9053	70.80
1.0247	3.60	1.3502	37.38	1.9209	71.42
1.0332	4.50	1.3669	38.82	1.9396	72.64
1.0393	5.20	1.3752	39.51	1.9610	73.60
1.0496	6.62	1.3895	40.62	1.9810	74.48
1.0553	7.37	1.4021	41.74	1.9953	75.08
1.0608	8.01	1.4155	42.82	2.0235	76.21
1.0710	9.33	1.4284	43.82	2.0625	77.66
1.0768	10.05	1.4306	44.02	2.0709	78.11
1.0904	11.66	1.4589	45.96	2.1160	79.95
1.0974	12.50	1.4663	46.45	2.1422	80.83
1.1040	13.48	1.4865	47.75	2.1599	81.59
1.1110	14.22	1.5012	48.61	2.1831	82.58
1.1231	15.54	1.5154	49.70	2.2008	83.11
1.1332	16.67	1.5281	50.55	2.2387	84.44
1.1438	17.79	1.5389	51.30	2.2552	85.10
1.1503	18.48	1.5590	52.50	2.2833	86.08
1.1561	19.07	1.5795	53.91	2.3117	87.35
1.1692	20.48	1.5870	54.42	2.3340	88.14
1.1818	21.81	1.6029	55.47	2.3762	89.50
1.1888	22.54	1.6112	56.07	2.4115	90.35
1.1993	23.63	1.6410	57.80	2.4360	91.50
1.2105	24.88	1.6498	58.45	2.4598	92.83
1.2210	25.94	1.6618	59.38	2.4765	93.42
1.2290	26.72	1.6937	60.73	2.4882	94.26
1.2356	27.31	1.7030	61.25	2.5144	95.28
1.2461	28.26	1.7169	62.00	2.5445	96.90
1.2546	29.00	1.7472	63.72	2.5647	97.66
1.2684	30.10	1.7641	64.37	2.5827	98.60
1.2813	31.40	1.7960	65.70	2.5925	99.20
1.2971	32.82	1.8042	66.06		
1.3028	33.30	1.8277	67.31		

Results from selenic acid prepared from lead selenate

1.0533	7.12	1.8898	70.12	2.2300	84.15
1.2429	28.06				

Interpolated results. Given at $\frac{20^\circ}{4^\circ}$ Vacuum

Specific gravity	Percent	Specific gravity	Percent	Specific gravity	Percent
1.000	—	1.210	24.84	1.420	43.16
1.005	0.9	1.215	25.30	1.425	43.56
1.010	1.56	1.220	25.84	1.430	43.94
1.015	2.12	1.225	26.30	1.435	44.32
1.020	2.92	1.230	26.84	1.440	44.52
1.025	3.62	1.235	27.28	1.445	45.00
1.030	4.16	1.240	27.70	1.450	45.32
1.035	4.70	1.245	28.18	1.455	45.68
1.040	5.32	1.250	28.58	1.460	46.04
1.045	6.08	1.255	29.06	1.465	46.36
1.050	6.66	1.260	29.44	1.470	46.70
1.055	7.34	1.265	29.82	1.475	47.01
1.060	7.92	1.270	30.26	1.480	47.32
1.065	8.56	1.275	30.76	1.485	47.66
1.070	9.20	1.280	31.26	1.490	47.98
1.075	9.82	1.285	31.74	1.495	48.28
1.080	10.44	1.290	32.18	1.500	48.54
1.085	11.02	1.295	32.64	1.505	48.92
1.090	11.62	1.300	33.08	1.510	49.30
1.095	12.20	1.305	33.50	1.515	49.68
1.100	12.88	1.310	33.92	1.520	50.02
1.105	13.58	1.315	34.36	1.525	50.34
1.110	14.14	1.320	34.82	1.530	50.68
1.115	14.66	1.325	35.26	1.535	51.04
1.120	15.20	1.330	35.72	1.540	51.38
1.125	15.74	1.335	36.10	1.545	51.66
1.130	16.32	1.340	36.43	1.550	51.98
1.135	16.86	1.345	36.88	1.555	52.28
1.140	17.38	1.350	37.34	1.560	52.56
1.145	17.90	1.355	37.80	1.565	52.88
1.150	18.44	1.360	38.24	1.570	53.28
1.155	18.92	1.365	38.66	1.575	53.56
1.160	19.48	1.370	39.10	1.580	53.94
1.165	20.02	1.375	39.50	1.585	54.30
1.170	20.58	1.380	39.98	1.590	54.62
1.175	21.08	1.385	40.06	1.595	54.92
1.180	21.60	1.390	40.66	1.600	55.28
1.185	22.22	1.395	41.10	1.605	55.62
1.190	22.66	1.400	41.56	1.610	55.96
1.195	23.18	1.405	41.98	1.615	56.30
1.200	23.70	1.410	42.36	1.620	56.60
1.205	24.26	1.415	42.78	1.625	56.88

Specific gravity	Percent	Specific gravity	Percent	Specific gravity	Percent
1.630	57.20	1.850	68.50	2.070	78.06
1.635	57.48	1.855	68.70	2.075	78.24
1.640	57.70	1.860	68.92	2.080	78.48
1.645	58.04	1.865	69.12	2.085	78.68
1.650	58.47	1.870	69.34	2.090	78.84
1.655	58.86	1.875	69.56	2.095	79.08
1.660	59.24	1.880	69.72	2.100	79.28
1.665	59.56	1.885	69.94	2.105	79.50
1.670	59.74	1.890	70.14	2.110	79.68
1.675	59.94	1.895	70.38	2.115	79.90
1.680	60.18	1.900	70.64	2.120	80.10
1.685	60.36	1.905	70.78	2.125	80.25
1.690	60.58	1.910	71.00	2.130	80.42
1.695	60.80	1.915	71.21	2.135	80.68
1.700	61.06	1.920	71.38	2.140	80.74
1.705	61.36	1.925	71.68	2.145	80.96
1.710	61.64	1.930	72.00	2.150	81.14
1.715	61.90	1.935	72.38	2.155	81.36
1.720	62.24	1.940	72.66	2.160	81.60
1.725	62.48	1.945	72.88	2.165	81.80
1.730	62.76	1.950	73.12	2.170	82.02
1.735	63.06	1.955	73.34	2.175	82.22
1.740	63.32	1.960	73.54	2.180	82.44
1.745	63.60	1.965	73.74	2.185	82.64
1.750	63.86	1.970	73.98	2.190	82.78
1.755	64.04	1.975	74.22	2.195	82.96
1.760	64.24	1.980	74.44	2.200	83.10
1.765	64.42	1.985	74.66	2.205	83.24
1.770	64.62	1.990	74.86	2.210	83.44
1.775	64.84	1.995	75.08	2.215	83.62
1.780	65.06	2.000	75.28	2.220	83.78
1.785	65.28	2.005	75.46	2.225	83.96
1.790	65.48	2.010	75.66	2.230	84.14
1.795	65.66	2.015	75.88	2.235	84.30
1.800	65.90	2.020	76.14	2.240	84.48
1.805	66.12	2.025	76.06	2.245	84.60
1.810	66.36	2.030	76.48	2.250	84.82
1.815	66.64	2.035	76.68	2.255	85.02
1.820	66.90	2.040	76.84	2.260	85.26
1.825	67.16	2.045	77.08	2.265	85.44
1.830	67.46	2.050	77.36	2.270	85.60
1.835	67.72	2.055	77.50	2.275	85.78
1.840	68.02	2.060	77.62	2.280	85.96
1.845	68.30	2.065	77.80	2.285	86.16

Specific gravity	Percent	Specific gravity	Percent	Specific gravity	Percent
2.290	86.38	2.395	89.96	2.500	94.64
2.295	86.60	2.400	90.10	2.505	94.80
2.300	86.82	2.405	90.20	2.510	94.96
2.305	87.04	2.410	90.30	2.515	95.32
2.310	87.26	2.415	90.46	2.520	95.58
2.315	87.46	2.420	90.74	2.525	95.86
2.320	87.66	2.425	91.00	2.530	96.10
2.325	87.84	2.430	91.24	2.535	96.41
2.330	88.00	2.435	91.46	2.540	96.68
2.335	88.18	2.440	91.70	2.545	96.92
2.340	88.34	2.445	92.00	2.550	97.12
2.345	88.48	2.450	92.28	2.555	97.30
2.350	88.66	2.455	92.56	2.560	97.48
2.355	88.82	2.460	92.85	2.565	97.68
2.360	88.98	2.465	93.02	2.570	97.94
2.365	89.14	2.470	93.20	2.575	98.20
2.370	89.30	2.475	93.36	2.580	98.46
2.375	89.48	2.480	93.68	2.585	98.70
2.380	89.60	2.485	94.02	2.590	99.04
2.385	89.72	2.490	94.32	2.595	99.36
2.390	89.84	2.495	94.48		

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MOLECULAR ATTRACTION. VIII PAPER

BY J. E. MILLS

I have occasionally seen and heard my previous papers upon the subject of molecular attraction[1] designated as "highly theoretical" papers. Such a statement, when it is applied to the papers as a whole, it seems to me, rests either upon an entire misconception of the relationship between fact and theory, or upon a very erroneous idea as to the content of the papers themselves. For the error involved in such a statement I feel myself largely responsible. I have failed to make sufficiently clear the boundary between the facts presented and the theory used, and I have moreover repeatedly referred to the "theory of attraction" presented, and thus unintentionally aided in the misconception. Moreover, the papers have been written as the work was completed and subsequent papers, while containing in themselves new material, contain also many additions and changes applicable to the papers that went before. I realize keenly that the entire set of papers should be revised. This revision is now made absolutely necessary by the fact that Dr. Sydney Young has just completed a revision of the volumes of the saturated vapor at the lower temperatures for the substances investigated by him, and this revision makes extensive, though usually small, alterations necessary in twenty-five of the substances examined. Dr. Young has also revised the Biot formulae used in eight of the substances examined. Dieterici[2] has also recently proposed an equation which throws much light upon, and is very similar in form to, the equation of Crompton which was studied in the previous papers of this series. For these reasons I am at present engaged upon a full and complete revision of the entire series of papers. But owing to the amount of work involved,

[1] Jour. Phys. Chem., **6**, 209 (1902); **8**, 383 (1904); **8**, 593 (1904); **9**, 402 (1905); **10**, 1 (1906); **11**, 132 (1907); **11**, 594 (1907).

[2] Drude's Ann., **25**, 569 (1908).

and to my wish to extend the work somewhat, the final republication cannot be attempted for a year or two. I see no reason for delaying publication of the new results obtained until that time. The object of this paper is therefore threefold: First, to call particular attention to the boundary between fact and theory so far as these papers are concerned; Second, to give a summary of the changes caused by the revisions made by Dr. Young in the data previously used; Third, to present the underlying fundamental equation in a new form—a form more simple and far more significant.

First.—Distinction between the Theory of Molecular Attraction and the Law Discovered by Means of the Theory

The work was based upon the belief that the total energy *per se* of a molecule must be the same in the liquid as in the gaseous state, the temperature being the same. If at a given temperature a given weight of gas represents more energy than the same weight of the substance as a liquid, the extra energy of the gas must be energy of position only (assuming no intramolecular change).

We have made no effort in any of our papers to prove this belief. It is not, however, a purely gratuitous assumption and the reasons leading to this belief were briefly outlined at the beginning of the sixth paper.[1] Expressing the above belief in a different form, we may say that the energy necessary to change a liquid into a gas must, then, be spent solely in overcoming the external pressure and in altering the distance apart of the molecules. (Unless the molecule breaks apart also or nears the point of disruption.)

Denoting the heat of vaporization by L, and the energy necessary to overcome the external pressure during the change from liquid to gas by E_e, $L - E_e$ must equal the energy spent in overcoming the molecular attraction.

Now is this amount of energy actually spent in overcoming the molecular attraction? In order to answer this question directly and definitely it would be necessary to

[1] Jour. Phys. Chem., 11, 132 (1907).

know the amount of the molecular attraction and the way in which this attraction varied with the distance apart of the molecules. Neither of these factors were known. But in this particular case the difficulty did not appear insurmountable. For we could *assume* the law of the attraction and obtain the *amount* of the attraction in a given case, and then find if the assumed law and the amount of the attraction found, were in accord with the facts under all other conditions. This is exactly what we proceeded to do. We assumed that the molecular attraction varied inversely as the square of the distance apart of the molecules and was a mutual property of each pair of molecules. Then from the internal heat of vaporization at one temperature and the assumed law we calculated the amount of the attraction. Having once found the amount of the attraction for the substance in question we proceeded to calculate the internal heat of vaporization at other temperatures and compare the calculated result with the observed in order to determine to what extent our supposition was in accord with the facts. After publishing the first paper we recognized that the test of the assumed law of the attraction could be more easily made, and more readily interpreted, if the quantities involved were combined into an equation having the form,

$$1. \qquad \frac{L - E_e}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant} = \mu'.$$

The derivation of this equation is given in the sixth paper above cited. L denotes the heat of vaporization at a certain temperature, E_e is the amount of energy spent in pushing back the external pressure as the liquid vaporizes. $L - E_e$ denotes, therefore, the internal heat of vaporization. d and D are the densities of liquid and saturated vapor respectively at the temperature in question. The constant we have called μ'.

The above equation 1, is, therefore, theoretically derived from the assumptions we have stated and in the manner detailed in the sixth paper above cited. And had we stopped

with the mere derivation of this equation our work would have deserved the criticism of being theoretical. But we proceeded to test the truth of the equation by reference to the facts. Assuming for the present (we review the proof below) that the facts were sufficient to establish the truth of the equation beyond reasonable doubt, then it is surely evident that the above equation represents a *fact* absolutely independently of the theory by which it was derived. *The above equation, if in accord with the facts, represents a law, not a theory.* If the equation is true it does not necessarily follow that the assumptions by which it was derived are true. The truth of the assumptions upon which the equation is based is rendered far more probable by the proof that the equation is true, but the assumptions are not thereby proved. We must distinguish, therefore, between the theory of molecular attraction advanced in these papers, and the law which was discovered by means of that theory. Now 99 percent of the work detailed in the papers under discussion, if not 99 percent of the words, had to do with *the proof of the law.* I am willing for any critic to attack the proof of the law as presented, but I am not willing for critics longer to class the law as theoretical merely because the law was theoretically derived, when it was afterwards established by direct reference to the facts.

It is as if a hunter concluded from certain tracks that there was a bear in a certain canebrake. So long as he does not go to the canebrake and look for the bear the existence of the bear in that canebrake is only a more or less probable theory. But if he goes to the canebrake and finds the bear, the existence of the bear at that point is a fact quite independent of the previous theory of the hunter upon the subject. The existence of the bear does not prove that he made the tracks which started the hunter upon his search. The tracks *might* have been made by some other bear.

If, however, the hunter follows the tracks carefully to the canebrake and then finds the bear, and only one bear, and the bear's feet fit the tracks observed, the hunter is justified

in supposing that his first conclusion with regard to the tracks was correct. It is for that reason that I am justified in examining the tracks as well as the bear—the theory as well as the law.

Second.—Proof of the Law, $\frac{L - E_e}{\sqrt[3]{d} - \sqrt[3]{D}}$ = Constant.

In testing the truth of the equation,

$$1. \qquad \frac{L - E_e}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant} = \mu',$$

thirty-eight substances have been examined. These are the only substances for which the proper measurements have been made. The measurements for thirty of the thirty-eight substances have been made by Sir Wm. Ramsay and Dr. Young, or by Dr. Young himself, or by Dr. Young and his co-workers, Thomas and Fortey, and the measurements for water are partly due to Sir Wm. Ramsay and Dr. Young. They measured at intervals of 10° C the vapor pressure of the liquid, the density of the liquid, and the volume of the saturated vapor, the measurements extending in most cases from 0° C to the critical temperature of the liquid. From this data the heat of vaporization could be calculated by means of the thermodynamical formula:

$$2. \qquad L = 0.0_{4}31833 \frac{dP}{dT} T(V - v) \text{ calories.}$$

Here T represents absolute temperature. The pressure is given in millimeters of mercury. V and v represent the volumes of 1 gram of the saturated vapor and of 1 gram of the liquid respectively. The $\frac{dP}{dT}$ was obtained from a Biot formula of the form,

$$3. \qquad \log P = a + b\alpha^t + c\beta^t,$$

in the manner described in a previous paper.[1] For the constants used see the reference just given, page 385.

[1] Jour. Phys. Chem., 8, 387 (1904).

The energy spent in overcoming external pressure, E_e, was calculated from the equation,

4. $$E_e = 0.0_{4}31833\ P(V - v) \text{ calories,}$$

where the constants and the letters have the meaning given above.

The densities of liquid and of vapor, d and D of equation 1 above, are obtained directly from the measurements, since the density is the reciprocal of the volume occupied by 1 gram.

Hence all of the values entering into equation 1 could be obtained with accuracy and the result of the test of this equation is given in the table below. A certain mean value of the constant μ' was rather arbitrarily chosen for each substance and these values are given at the top of the table. All values of the constant which show a divergence of more than 2 percent from this mean value are marked by an asterisk. The average value of the results not so marked for each substance was then obtained and is given at the bottom of the table. All results that show a greater divergence from this average value than 1 percent are marked with a + or —, above and to the left, to denote the excess or deficiency of the value.

A cursory examination of the table verifies at once the substantial truth of the equation for most of the substances examined. Thus of the first twenty-six substances shown in the table, excepting the results at 0° C and near the critical temperature, there is not a single divergence from the average value of the constant greater than 2 percent except with diisobutyl. A detailed examination of the results is however necessary to show the real significance of this agreement.

TABLE I

Mean μ'	Ethyl oxide 103.8	Di-iso-propyl 96.48	Di-iso-butyl 87.72	Isopen-tane 105.5	Normal pentane 110.0	Normal hexane 102.80
Temperature 0° C	+ 105.6	97.8	+ 89.1	+ 107.2	+ 111.1	103.6
10	+ 104.8	—	—	104.5	—	—
20	103.9	—	—	105.1	—	—
30	103.4	—	—	105.1	— 108.6	—
40	103.0	—	—	104.8	109.4	—
50	102.9	97.9	—	104.7	109.3	—
60	102.9	97.9	—	104.5	109.6	102.4
70	102.7	98.0	—	104.4	109.7	102.7
80	102.9	98.1	—	105.0	109.8	103.0
90	103.2	97.8	87.9	105.4	109.9	103.0
100	103.6	97.6	87.4	105.9	110.0	103.1
110	103.8	97.5	86.8	106.0	110.5	103.4
120	104.1	97.6	— 86.0	106.3	+ 111.1	103.5
130	104.6	97.5	— 86.0	106.5	111.0	103.4
140	+ 105.0	97.5	— 84.9*	+ 106.7	110.5	103.0
150	+ 105.1	97.5	— 84.7*	+ 106.9	110.5	103.1
160	104.6	97.7	— 85.0*	+ 106.7	110.3	102.5
170	103.5	97.7	— 85.6*	105.5	110.3	102.4
180	— 101.9	98.0	86.2	— 103.4	109.3	102.6
190	— 97.4*	98.1	86.8	—	— 106.3*	102.8
200	—	98.1	87.0	—	—	102.7
210	—	97.3	87.3	—	—	102.1
220	—	— 94.8	87.9	—	—	— 101.1
230	—	—	+ 88.6	—	—	98.0*
240	—	—	+ 89.0	—	—	—
250	—	—	+ 89.5	—	—	—
260	—	—	+ 89.4	—	—	—
270	—	—	87.6	—	—	—
280	—	—	—	—	—	—
290	—	—	—	—	—	—
Critical temperature	193.8°	227.35°	276.8°	187.8°	197.2°	234.8°
Average μ'	103.76	97.53	87.58	105.46	109.94	102.80
μ' from $\frac{dP}{dT} = \frac{2R}{V}$	102.0	96.5	80.7	107.0	109.4	99.2

TABLE I—(*Continued*)

Mean μ'	Normal heptane 98.2	Normal octane 92.78	Hexa-methylene 103.63	Benzene 109.23	Fluo-benzene 85.65	Chlor-benzene 81.42
Temperature						
0° C	99.6	+* 97.5	102.6	108.3	85.0	+* 83.8
10	—	—	—	—	—	—
20	—	—	—	—	—	—
30	—	—	—	—	—	—
40	—	—	—	—	—	—
50	—	—	—	—	—	—
60	—	—	—	—	—	—
70	98.7	—	—	108.7	—	—
80	99.3	—	104.3	109.2	+ 86.8	—
90	99.2	—	104.3	109.1	+ 86.8	—
100	98.9	—	104.1	108.7	+ 86.9	—
110	98.6	—	103.9	108.3	86.4	—
120	98.2	92.6	103.4	— 107.6	86.1	—
130	97.7	92.9	103.0	107.9	85.8	— 79.9
140	— 97.4	92.7	102.9	108.2	85.3	— 80.3
150	— 97.2	92.5	— 102.5	108.5	84.9	— 80.7
160	97.4	92.7	102.8	109.1	84.7	80.9
170	97.7	92.4	102.7	109.4	84.8	81.1
180	98.5	92.7	103.4	110.1	84.9	81.5
190	98.9	92.8	102.9	110.1	84.8	81.5
200	99.2	93.9	103.1	110.1	84.9	81.6
210	+ 99.7	93.9	103.5	+ 110.7	85.3	81.7
220	+ 99.7	93.6	104.2	+ 110.5	85.7	82.2
230	+ 99.8	93.9	104.6	+ 110.4	85.9	82.4
240	+ 99.8	93.7	104.6	+ 110.4	86.3	+ 82.8
250	99.3	+ 94.2	+ 104.9	+ 110.5	+ 86.6	+ 82.9
260	— 96.6	+ 94.6	104.7	110.2	+ 86.6	+ 82.7
270	—	+ 94.3	103.4	109.3	85.8	82.5
280	—	93.4	—	— 107.8	— 84.0	—
290	—	— 91.0	—	—	—	—
Critical temperature	266.90°	296.2°	280.0°	288.5°	286.55°	359.1°
Average μ'	98.64	93.16	103.63	109.26	85.65	81.66
μ' from $\frac{dP}{dT} = \frac{2R}{V}$	90.8	84.2	104.5	110.5	85.2	81.3

TABLE I—(*Continued*)

Mean μ'	Brom-benzene 55.37	Iodo-benzene 43.46	Carbon tetra-chloride 44.29	Stannic chloride 26.51	Methyl formate 119.86	Ethyl formate 107.14
Temperature						
0° C	—	—	— 43.5	— 26.2	+ * 123.9	+ 108.8
10	—	—	—	—	—	—
20	—	—	—	—	—	—
30	+ * 57.6	+ 44.2	—	—	+ 122.1	—
40	—	—	—	—	+ 121.4	—
50	—	—	—	—	121.0	+ 108.5
60	—	—	—	—	120.3	+ 108.4
70	—	—	— 43.5	—	119.6	108.2
80	—	—	— 43.5	—	119.4	107.8
90	—	—	— 43.6	—	119.4	107.5
100	—	—	— 43.5	26.7	119.1	107.4
110	—	—	— 43.5	26.7	119.7	107.3
120	—	—	— 43.5	26.7	120.1	107.1
130	—	—	— 43.4	26.7	119.8	106.9
140	—	—	— 43.5	26.5	119.8	106.9
150	— 54.6	—	43.5	26.5	119.7	106.5
160	— 54.6	—	43.8	26.5	119.2	— 106.5
170	— 54.8	—	44.0	26.5	— 119.1	106.0
180	55.0	— 42.7	43.9	26.5	— 118.1	— 106.4
190	55.2	42.9	44.0	26.4	— 116.4 *	— 106.0
200	55.4	43.1	44.2	26.3	— 113.3 *	— 105.1
210	55.7	43.3	44.3	26.4	— 106.6 *	— 103.8 *
220	55.9	43.5	+ 44.5	26.4	—	— 101.3 *
230	56.0	43.6	+ 44.8	26.5	—	— 97.6 *
240	55.8	43.6	+ 44.9	26.5	—	—
250	55.8	43.6	+ 45.2	26.5	—	—
260	+ 56.1	43.4	+ 45.0	26.5	—	—
270	+ 56.2	43.2	+ 44.5	26.4	—	—
280	—	—	43.9	26.4	—	—
290	—	—	—	—	—	—
Critical temperature	397°	448°	283.15°	318.7°	214.0°	235.3°
Average μ'	55.47	43.37	44.01	26.51	119.86	107.14
μ' from $\frac{dP}{dT} = \frac{2R}{V}$	56.3	43.8	45.3	25.9	119.8	103.9

TABLE I—(*Continued*)

Mean μ'	Methyl acetate 108.8	Propyl formate 98.79	Ethyl acetate 98.0	Methyl propionate 99.02	Propyl acetate 92.30
Temperature 0° C	110.7	+ 100.8	+ 102.2*	— 97.8	+ 97.1*
10	—	—	—	—	—
20	—	—	—	—	—
30	—	—	—	—	—
40	—	—	—	—	—
50	110.3	—	—	—	—
60	110.7	—	—	—	—
70	110.6	+ 100.0	99.3	99.9	—
80	110.5	+ 100.3	99.6	99.8	—
90	109.9	99.5	99.8	99.8	94.0
100	109.7	99.1	99.9	99.3	93.8
110	109.6	98.8	99.9	99.2	94.0
120	109.6	98.5	99.7	99.1	93.9
130	109.6	98.4	99.2	99.1	93.5
140	109.7	98.5	99.2	98.9	93.2
150	109.9	98.0	98.6	98.9	93.2
160	109.8	97.8	98.2	98.9	93.3
170	109.5	97.6	98.6	98.6	93.0
180	108.8	97.8	98.6	98.8	93.2
190	108.5	98.5	98.7	99.1	93.2
200	108.2	98.5	98.9	99.5	93.2
210	107.0	98.4	98.7	99.4	93.3
220	105.0*	99.2	97.7	99.4	93.2
230	100.4*	99.5	96.5	98.8	92.8
240	—	99.0	94.0*	97.1	92.5
250	—	97.6	—	93.9*	92.2
260	—	95.0*	—	—	90.7
270	—	—	—	—	86.5*
280	—	—	—	—	—
290	—	—	—	—	—
Critical temperature	233.7°	264.85°	250.1°	257.4°	276.2°
Average μ'	109.59	98.79	98.88	99.02	93.12
μ' from $\frac{dP}{dT} = \frac{2R}{V}$	103.6	93.7	91.7	92.4	84.1

TABLE 1—(*Continued*)

Mean μ'	Ethyl propionate 91.97	Methyl butyrate 91.17	Methyl isobutyrate 87.78	Water 558.1	Methyl alcohol 302.3	Ethyl alcohol 240.1
Temperature 0° C	+96.1*	+96.5*	+92.5*	+574.7*	304.7	−232.8*
10	—	—	—	+571.4*	306.0	−235.4
20	—	—	—	+567.5	306.6	−237.4
30	—	—	—	+564.1	307.9	239.9
40	—	—	—	+561.5	307.4	241.7
50	—	—	—	559.1	+308.3	242.4
60	—	—	—	556.7	308.0	+243.6
70	—	—	—	554.9	308.1	+244.1
80	—	—	—	553.4	307.8	+244.9
90	+93.1	—	89.2	552.4	307.1	+244.6
100	+93.5	90.9	89.3	551.3	306.3	+244.8
110	+93.2	90.8	89.0	550.0	306.0	242.7
120	+93.0	90.8	88.7	−548.4	305.4	242.1
130	92.5	90.6	88.8	−547.5	304.5	241.0
140	91.7	91.0	88.8	−547.1	−304.1	241.0
150	91.3	91.0	88.6	−547.1	301.3	241.1
160	−90.9	90.8	88.4	−547.4	303.1	239.8
170	−90.6	90.7	88.3	548.6	−302.3	−238.2
180	−90.4	90.9	88.3	549.9	−300.9	−236.5
190	90.6	91.2	88.5	552.0	−300.8	−233.3*
200	90.7	91.7	88.9	554.3	−299.3	−230.0*
210	91.1	91.9	89.0	554.8	−295.4*	−226.3*
220	91.4	91.8	88.9	560.4	−287.6*	−223.0*
230	91.4	+92.3	88.8	+561.0	−276.5*	−219.7*
240	91.5	+92.4	88.3	+562.1	−237.4*	−209.2*
250	91.4	+93.0	87.7	+560.9	—	—
260	−90.4	+92.5	−86.2	558.3	—	—
270	86.7*	91.2	—	+561.2	—	—
280	—	84.2*	—	—	—	—
Critical temperature	272.9°	281.3°	267.55°	370°	240.0°	243.1°
Average μ'	91.59	91.31	88.45	555.1	305.04	240.90
μ' from $\frac{dP}{dT} = \frac{2R}{V}$	80.8	84.3	82.0	—	262.4	179.9

TABLE I—(*Continued*)

Mean μ'	Propyl alcohol 199.2	Acetic acid	Carbon disulphide 82.41	Chloroform 57.97	Acetone 150.8
Temperature					
0° C	+203.1	—	82.2	58.0	150.8
10	—	—	82.4	57.9	150.7
20	—	81.3	82.5	57.8	150.7
30	—	83.8	82.6	57.8	150.8
40	—	86.1	82.7	57.4	149.7
50	—	87.8	82.8	57.9	151.1
60	—	90.4	82.8	58.0	151.2
70	—	92.2	82.8	—	—
80	199.9	94.7	82.8	—	—
90	199.2	96.4	82.7	—	—
100	197.6	98.5	82.6	+59.0	151.3
110	196.2	100.7	82.5	—	—
120	193.6*	104.3	82.2	—	—
130	191.3*	104.9	81.9	—	—
140	191.1*	105.5	81.6	—	—
150	187.8*	106.6	81.2	—	—
160	185.6*	107.9	—	—	—
170	184.1*	111.7	—	—	—
180	182.7*	111.3	—	—	—
190	180.4*	113.3	—	—	—
200	178.6*	115.4	—	—	—
210	176.6*	117.5	—	—	—
220	173.2*	119.1	—	—	—
230	168.8*	121.5	—	—	—
240	164.1*	124.1	—	—	—
250	160.2*	126.4	—	—	—
260	157.0*	128.4	—	—	—
270	—	130.0	—	—	—
280	—	131.2	—	—	—
290	—	131.2[1]	—	—	—
Critical temperature	263.7°	321.65°	273.05°	260.0°	237.5°
Average μ'	199.2	—	82.41	57.97	150.8
μ' from $\frac{dP}{dT} = \frac{2R}{V}$	143.7	150.7	98.8	—	—

[1] At 300° = 130.0; 310° = 127.4; 320° = 122.2.

TABLE I—(*Continued*)

Mean μ'	Ammonia 381.9	Sulphur dioxide 85.80	Sulphur dioxide 85.80	Carbon dioxide 95.2	Nitrous oxide 88.3
Temperature					
— 30° C	381.3	—	—	94.6	—
— 20	380.9	—	—	$\overset{+}{96.3}$	$\overset{-}{82.5}$*
— 10	380.6	$\overset{+}{87.4}$	$\overset{+}{88.6}$*	95.8	$\overset{-}{87.0}$
0	380.5	$\overset{+}{86.8}$	$\overset{+}{87.0}$	95.4	$\overset{+}{90.7}$*
10	381.1	84.2	$\overset{-}{85.5}$	$\overset{-}{93.7}$	$\overset{+}{90.5}$*
20	382.2	84.1	$\overset{-}{84.3}$	$\overset{-}{90.5}$*	$\overset{-}{84.9}$*
30	383.2	84.4	$\overset{-}{82.7}$*	$\overset{-}{61.4}$*	$\overset{-}{62.5}$*
40	385.1	84.6	$\overset{-}{81.1}$*	—	—
50	—	$\overset{-}{81.6}$*	$\overset{-}{80.1}$*	—	—
60	—	$\overset{-}{83.0}$*	$\overset{-}{77.8}$*	—	—
70	—	85.8	—	—	—
80	—	$\overset{+}{88.1}$*	—	—	—
90	—	$\overset{+}{88.9}$*	—	—	—
100	—	$\overset{+}{87.5}$*	—	—	—
110	—	$\overset{+}{86.6}$	—	—	—
120	—	$\overset{+}{87.6}$*	—	—	—
130	—	$\overset{+}{89.2}$*	—	—	—
140	—	$\overset{+}{91.4}$*	—	—	—
150	—	$\overset{+}{94.2}$*	$\overset{+}{95.3}$*	—	—
Critical temperature	131.0°	156.0°	156.0°	31.35°	38.8°
Average μ'	381.86	85.48	85.6	95.16	—
μ' from $\frac{dP}{dT} = \frac{2R}{V}$	—	85.4	85.4	91.8	93.6

The magnificent series of measurements made by Dr Young and his co-workers, stand for accuracy in a class to themselves, and the thirty-one substances for which their

measurements are available are placed first in the table above. In examining the data for these substances in detail we would point out:

(1) At 0° C, except for ethyl oxide, and at 30° C for brom-benzene and iodo-benzene, the calculated density of the vapor had to be used. The equation used for this calculation was

$$4. \qquad D = 0.0_4 16014 \frac{Pm}{T}.$$

The error introduced into the constant by this calculation varies with the reduced temperature[1] $\left(\frac{273}{T_c}\right)$ for the substance in question and makes the value of the constant at 0° C too large. The error thus introduced may even reach 2 percent as with isopentane.

(2) The calculation of the $\frac{dP}{dT}$ introduces the largest error into the constant, and is especially uncertain at the end-points of the vapor pressure curve. This point has already[2] been discussed and it is useless to repeat that discussion here. In addition to this source of error we have also pointed out[3] that the Biot formula from which the $\frac{dP}{dT}$ is derived cannot be made to fit the observed pressures exactly, in the neighborhood of the critical temperature, but always gives too low results. This error is greatly magnified in the calculation of the $\frac{dP}{dT}$ and results invariably in giving too low values for the constant as the critical temperature is approached. *The values at 0° C (30° C for brom-benzene and iodo-benzene), and in the immediate neighborhood of the critical temperature, must, therefore, be excluded from consideration because of errors introduced by the calculation.*

(3) Water, the alcohols, and acetic acid, are known

[1] Young: Stoichiometry, page 342, etc.
[2] Jour. Phys. Chem., 8, 394–397 (1904).
[3] Ibid., 9, 406–411 (1905).

to be associated liquids and must be left out of consideration since for associated liquids equation 1 is not theoretically true.

(4) As regards di-isobutyl, suspicion as to the purity of the substance was caused by finding in 1906 that some small whitish crystals had formed in the original carefully preserved di-isobutyl measured by Young and Fortey in 1900. On pouring off the clear di-isobutyl, about 50 cc, and attempting to redistil the same through a Young's fractionation column, fresh similar crystals formed in small amounts in and throughout the stillhead, appearing even in the condensing tube, the boiling point of the di-isobutyl meanwhile remaining perfectly constant. The cause of this rather remarkable and unexpected appearance of crystals we did not have time to investigate, the amount of the crystals obtained from the liquid at hand being too small to permit of their investigation. It is possible that the di-isobutyl may have contained some of these crystals at the time of its original examination by Dr. Young. Dr. Young used extreme care to procure pure liquids for investigation, but the remarkable fact that the formation of the crystals did not alter the boiling point of the di-isobutyl appreciably and could not be separated from it by fractional distillation might have allowed small amounts of this impurity to have escaped detection. Until further investigation can definitely settle this point, the fact that di-isobutyl does show four divergences greater than 2 percent from the average value of the constant should not be given too great weight.

(5) Excepting, therefore, the values at 0° C (30° C for brom-benzene and iodo-benzene), and near the critical temperature, and the substances water, the alcohols, acetic acid, and di-isobutyl for the reasons stated, there is not a single divergence greater than 2 percent from the average constant shown by the equation for the remaining twenty-five substances investigated by Young and his co-workers. Out of the 431 comparisons within these limits possible for these 25 substances there are only 17 that show a greater divergence

than 1.5 percent from the average value of the constant. And of the twenty-five substances there are eight that show not a single divergence, within the limits stated, greater than 1 percent.

(6) It can be affirmed without hesitation that the equation is as accurate as the observations will permit, for the equation has proved itself more accurate than the observations formerly available. If the table given in this paper be compared with the tables previously given[1] numerous slight changes will be observed. These alterations have been caused by the following changes: Young has resmoothed[2] the volumes of the saturated vapor at low temperatures for all of the non-associated substances mentioned above except ethyl ether. Also he has recalculated more accurate constants for the Biot formulae for ethyl ether, fluo-benzene, chlor-benzene, brom-benzene, iodo-benzene, ethyl propionate, methyl butyrate, and methyl isobutyrate. I have used for benzene values for the heat of vaporization obtained directly from the data given by Young instead of the values given by Tsuruta. I also discovered a gross error in my calculations for stannic chloride. For this error and my former statements regarding the possible error in the measurements for stannic chloride I apologize most heartily to Dr. Young. A few misprints in the data have been brought to light.

Now the changes above-mentioned have served to eliminate the larger divergences before shown by the equation and make the constants given by the equation very much more regular. Therefore these revisions are a triumph for the law expressed in equation 1—*it was more accurate than the data available.*

We do not wish this statement misunderstood. Each value of the constant depends upon four measurements, temperature, vapor pressure, density or volume of the liquid, and density or volume of the saturated vapor. The errors

[1] Jour. Phys. Chem., **8**, 397–398 (1904); **10**, 17 (1906); **11**, 611 (1907).
[2] See Arrhenius number of Zeitschrift für phys. Chemie.

in these measurements are always combined and often greatly multiplied in their effect upon the constant. This multiplication of error is very serious in calculating the intermediate value $\frac{dP}{dT}$, since an error in the vapor pressure is multiplied from 10–70 times if it exerts its full effect upon the $\frac{dP}{dT}$. Assuming equation 1 exactly true, the fact that the measurements can give a constant practically to within 1.5 percent in spite of this combination and multiplication of error is a high tribute to the wonderful accuracy of the measurements themselves. In order to have produced a constant accurate to within 1.5 percent the individual measurements must have possessed a far greater proportionate accuracy as already explained and discussed.[1]

There is every reason to believe that the remaining divergences are due to the measurements. Thus every one of the 17 divergences greater than 1.5 percent occurring as above mentioned in the 25 substances occur at the very points where known errors are greater. These divergences are as follows: normal octane, 260; chlor-benzene, 130, 140, 250; brom-benzene, 150, 160; iodo-benzene, 180; carbon tetrachloride, 230 to 260; methyl formate, 30; ethyl propionate, 90 to 120; methyl butyrate, 250. These divergences occur either as + or — divergences at the lowest temperatures for which the volumes of the saturated vapor were measured and are due to the uncertainty of that measurement, or they occur as positive divergences not far below the critical temperature where they are introduced because of a "backward positive kick" introduced into the Biot formula in trying to make it fit the vapor pressure curve near the critical temperature.

If the constant of equation 1 varied because the equation were not exactly true, such regular divergence, if it amounted to more than 1/2 of 1 percent, would make itself apparent by causing a regular variation in the + or — diver-

[1] Jour. Phys. Chem., **8**, 392–397 (1904).

gences greater than 1 percent as marked in the table. No such regular variation can be detected.

(7) For the last seven substances shown in the table the data obtainable are not always trustworthy. These results are taken unchanged from the original paper[1] and the detailed discussion can be there followed. We would only say that, in our opinion, in all of these cases the equation shows a constant to within the limit of accuracy of the data used.

(8) In a previous paper[2] we have shown reasons for believing that at the critical temperature,

$$5. \qquad \frac{dP}{dT} = \frac{2R}{V_c}.$$

Here R is the usual gas constant and is equal to $\frac{62430}{m}$ if the $\frac{dP}{dT}$ is to be obtained in millimeters of mercury. Substituting this value in equation 2, and replacing L and E_e of equation 1 by their values as given in equations 2 and 4, we have at the critical temperature, where d = D and v = V, the equation,

$$6. \quad \mu' = 3 \times 0.0_{4}31833V^{1/3}(2RT-PV) = V^{1/3}\left(\frac{11.924T}{m} - 0.0_{4}955PV\right).$$

We have calculated the values for μ' at the critical temperature from this equation and give the values at the bottom of Table 1. A comparison of these values with the average values of μ' given just above them shows that equation 6 possesses much interest. In many cases the agreement is within the limit of experimental error. But considerable divergence is shown with di-isobutyl, normal heptane, normal octane, the esters, and associated liquids, and it would therefore seem that equation 5 is not always true. We expect to discuss these interesting relations in a later paper.

From the facts that have been presented we draw the conclusion that equation 1 is true for normal non-associated

[1] Jour. Phys. Chem., 10, 1 (1906).
[2] Ibid., 9, 402–406 (1905).

liquids, and the evidence presented is sufficient, we believe, to justify the claim that the equation, $\frac{L - E_e}{\sqrt[3]{d} - \sqrt[3]{D}}$ = constant, represents a new and most exact law.

Third.—Statement of the Law in a Simpler Form.

The equation above has been investigated only for the change of a substance from the state of liquid to that of saturated vapor, while under its own vapor pressure. Throughout these conditions the equation represents a relation between molecular forces and it would seem extremely unlikely that these molecular forces obey one law at one time, or under one condition, and another aw at another time, or under another condition. Taking, therefore, into consideration the theory by which the equation was derived, it is certainly probable that the equation will represent under all circumstances the work done against the force of molecular attraction in moving molecules further apart. Now the further the molecules are moved apart the less becomes the value of D, and D will finally become zero when the molecules have been moved an infinite distance apart. Making, therefore, D equal to zero, and calling $L - E_e$, λ, we can then put the equation under discussion into the form, $\frac{\lambda}{\sqrt[3]{d}}$ = constant. Now the distance apart of the molecules which we will call s, is proportional to $\sqrt[3]{\frac{v}{n}} = \frac{1}{\sqrt[3]{nd}}$ where n represents the number of molecules and is therefore a constant. We may therefore write,

$$7. \qquad \lambda s = \text{constant},$$

as the very simple form assumed by the law under discussion. This statement means simply this:

In any normal substance the internal heat given out as the molecules approach each other, multiplied by the distance apart of the molecules, is equal to a constant.

Equation 7 is very suggestive when alone considered, and when combined with certain other known laws gives rise

to some unexpected relationships; relationships so unexpected that we are not willing to undertake their discussion at the present time. We hope that some work already undertaken will give us a further insight into the nature of the relationships involved and we will then return to a further discussion.

In conclusion, the author desires to express his indebtedness to Dr. Sydney Young for his kindness in sending the revised data used in this paper in advance of its publication, and for supplying many details with regard to the measurements. The trouble and work involved can only be fully understood by the author, and we here express the sincere thanks which we have very often had occasion to feel. Dr. Young expects shortly to publish in the Proceedings of the Royal Dublin Society the full data upon which these calculations are based.

University of North Carolina,
Chapel Hill, N. C.
May 7, 1909

AN EASY METHOD FOR DETERMINING VAPOR-DENSITIES

BY PHILIP BLACKMAN

PART I

The apparatus here described has to be especially made, but is then always ready for use. It is more suitable for experimenting upon liquid substances than upon solids.

It consists of a long capillary tube, from 300–400 cm in length (the longer the better), bent into the form of a closed W (or with still more folds) so that it occupies as little length as possible and at the same time presents a compact form. It is open at both ends with a tap at one end. The total length of tube must be carefully graduated in cubic centimeters divided into millimeters (in an accurate piece of apparatus the divisions should be in the ratio of the relative corresponding internal volumes of the bore, especially in the neighborhoods of the bends).

Some mercury is placed in a small vessel, and covered with a layer of the substance to be experimented on. The tap-end of the capillary is placed into the mercury, the tap being open, and a short thread (1 or 2 cm) of the metal is sucked up; the capillary is raised till the end dips into the layer of substance above and some of it (4–7 mm) drawn in; the capillary is now at once lowered into the mercury and a second length of it sucked up, sufficient to close the tap completely, which is then shut off.

The length of the thread of substance is carefully measured, and the capillary (except the tap) completely surrounded by a suitable heating jacket, and heated in a horizontal position in the vapor of some substance boiling at a temperature above that at which the substance experimented upon boils at ordinary pressures. When the substance in the bore has completely vaporized and the movable mercury thread has come to rest, the length of the capillary from one

mercury-thread to the other is determined (see Fig. 1). The atmospheric pressure and vaporizing temperature are required known.

Fig. 1

Let

l = the length of the thread of substance introduced;
L = the length of the thread of vaporized substance;
t_2 = the temperature of the heating medium;
s = the specific gravity (as measured on the metric system) of the substance when introduced into the capillary;
p = the atmospheric pressure;
d = the vapor density required;
α = the area of the cross-section of the bore of the capillary tube (this is not required to be known).

The weight of the substance introduced $= sl\alpha \ldots\ldots (1)$; its volume at $t_2°$ and pressure $p = L\alpha$, which at 0° and 760 mm. pressure $= \frac{273\, pL\alpha}{760(273 + t_2)} \ldots\ldots (2)$; hence its density = (1) ÷ (2), or, if compared with hydrogen at 0° and 760 mm pressure (assuming that 1 gram of hydrogen occupies 11160 cc.)

$$d = 11160\,(1) \div (2)$$
$$= \frac{31068\, sl(273 + t_2)}{pL}.$$

PART II

If the tap end of the apparatus be bent *at right angles to the plane* of the rest of the apparatus (otherwise bending it will render it impossible for the movable mercury-thread to be seen or the readings to be observed), the apparatus will admit of its being heated in a thermostat to any desired temperature, a method of procedure which will in many cases or for special purposes be found much more convenient and

advantageous than a heating-jacket-method. With this apparatus the mercury-thread closing the tap must be long enough to fill the whole of the right-angled bend. Also the formula to be employed in the calculation of results obtained with this apparatus is more correctly written

$$d = \frac{31068\, sl(273 + t_2)}{\left(p + \frac{\delta\Delta}{13.6}\right)L},$$

in which δ = the specific gravity of the heating liquid, Δ = the depth of the movable mercury-thread below the surface of the heating medium, and 13.6 = the specific gravity of mercury. It is as well however to point out that the quantity $\delta\Delta/13.6$ will rarely amount to as much as 1 mm, and may for all practical purposes be neglected and the less complicated formula used.

The tap-end must be outside the heating medium. The other, open end of the apparatus may be immersed in the liquid, though of course the apparatus may be so made that this end too is at right angles to the plane of the rest of the apparatus and thus projects outside the heating liquid (in which case the quantity $\delta\Delta/13.6$ becomes unnecessary), but very little advantage will be gained by this.

Neither apparatus can be used with substances which act upon mercury. At high temperatures p must be written $p - q$, where q is the vapor-tension of mercury. The mercury employed must be quite clean. Every time before an experiment is performed the apparatus must be thoroughly cleaned and dried. When the movable mercury-thread comes to rest at an upright (not horizontal—this applies only to the apparatus in Part I if placed so that the plane of the apparatus is vertical and not horizontal) bend, p must be written $p + m$, m being the vertical distance of one end of that thread above the other end; to avoid the possibility of this occurring and the consequent correction, care should be taken that before heating the apparatus is in such a position that its plane lies horizontally.

Results.—It is not at all a difficult matter to measure l correctly to fourths or even fifths of a mm by the use of an ordinary magnifying glass held over the scale and the thread to be measured. In connection with this it must be borne in mind that the chief source of error lies in the accurate determination of l. In very exact work an allowance in l (which, however, is very small) must be made for the convexivity of the mercury ends contiguous to the thread of substance.

In all cases here given $t_2 = 100°$.

Substance	s	l mm.	p mm.	L mm.	d	
					Found	Theory
CH_3I	2.281	4.2	750	2161	68.5	70.9
C_2H_5I	1.934	5.8	750	2259	75.5	77.9
C_2H_5Br	1.425	5.5	741	2300	53.3	54.5
$C_2H_4Cl_2$	1.240	5.6	741	2216	49.0	49.4
$CH_3.CO_2C_2H_5$	0.908	5.6	746	1914	41.9	44.0
$CHCl_3$	1.495	5.8	746	2279	58.2	59.7
$C_5H_{11}.NO_2$	0.895	8.8	746	2192	56.6	58.5
C_6H_6	0.880	6.0	751	2100	38.8	39.0

PART III

The apparatus here described, though more expensive to make than those already detailed, will however be found to possess these important advantages, which will more than repay the initial cost of manufacture. These advantages are that:

(1) Greater accuracy can be obtained in the measurement of l, because the thread of substance introduced may be made several cm long.

(2) The apparatus need not necessarily be of great length (120 cm in length is quite sufficient, if not more than 1 cm length of the thread of substance be introduced), though the longer the length of the capillary tube is the greater l may be made and thus increased accuracy is obtained.

Apparatus.—The bore of the capillary tube, 8–10 cm on either side of the tap, should be of a *very small diameter*, the

rest of the capillary tube having a *comparatively large diameter* (of course the bore of the latter must not be too wide that a thread of mercury cannot remain unbroken in it). The radius, r, of the cross-section of the narrower bore, and the radius, R, that of the larger bore, must be accurately known, these being permanent constants for any one piece of apparatus. As to the method for graduating the total length of the capillary tube, the general direction already given in Part I apply here.

Method.—Mercury is drawn in until the whole of the narrow bore and 1 or 2 cm of the beginning of the wider bore are filled. This is immediately followed by a thread, several cm long, of the substance to be experimented on, and behind this another thread of mercury to close the tap is drawn in, after which l is measured. The apparatus is heated, and the lengths l_c of the narrower bore and L of the wider bore occupied by the vapor are determined.

Formulae.—The weight of substance $= \pi r^2 ls$, and the volume occupied by the vapor $= \pi r^2 l_c + \pi R^2 L$. Substituting these values for the quantities $sl\alpha$ and $L\alpha$ respectively in the theoretical portion given in Part I,

$$d = \frac{31068\, r^2 ls(273 + t_2)}{p(r^2 l_c + R^2 L)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1).$$

As r is small in comparison with R, $r^2 l_c$ is very small compared with R^2L, and is consequently a negligible quantity for all ordinary purposes. This consideration admits of the simplification of the formula to

$$d = \frac{31068\, r^2 ls(273 + t_2)}{pR^2 L} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2).$$

In practice it may be of great advantage to calculate beforehand for any one apparatus the quantities r^2 and R^2, and further work out the quantity $31068r^2/R^2$, say equal to the known factor K, which is used as a constant for that

particular apparatus, and the simpler, and almost scarcely less accurate, formula can now be written

$$d = \frac{Kls(273 + t_2)}{pL} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3).$$

In conclusion, I must once more offer my sincere thanks to R. Blair, Esq., Education Officer to the London County Council, and to the authorities of the Hackney Technical Institute for the continued facilities granted to me to carry out research work.

London, N. E. (England)

THE ELECTROCHEMISTRY OF LIGHT. VIII

BY WILDER D. BANCROFT

The Theory of Solarization. Part II

Liesegang[1] has coined the word "pseudo-solarization" to describe cases in which both a positive and a negative image occur on the plate, the positive being the more dense. Lüppo-Cramer[2] considers that there are numerous instances of pseudo-solarization and he describes the matter as follows:

"Eder[3] first noticed that a reversal was obtained with a normally exposed plate when hyposulphite was added to the ferrous oxalate developer. Kogelmann[4] observed the same phenomenon when a good deal of ammonia was added to a metol or an amidol developer.[5] Liesegang offered an explanation to which we shall return later.

"Recently Adrien Guébhard has made a careful study of reversals on normally exposed plates in his interesting and illustrated papers: 'Inversion de l'image sous-posée par sur-développement lent,'[6] 'Un mode nouveau d'inversion photographique'[7] and 'Sur l'inversion photographique.'[8] This investigator mentions often the appearance of the dichroic fog in connection with the phenomenon; but does not have in his solutions the conditions which other authors have believed to be absolutely essential. The reason for the solution of silver bromide in Guébhard's experiments or for the reduction of silver bromide to colloidal silver, to speak more generally, is evidently the great dilution of the developer.

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[1] Phot. Correspondenz, 1895, 558.

[2] Photographische Probleme, 184 (1907).

[3] Eder's Handbook der Photographie, 5th Ed., 3, I, 114 (1902).

[4] Eder's Jahrbuch der Photographie, 13, 379 (1899).

[5] Cf. also Reeb. Bull. Soc. Franç. (2), 21, 207 (1905).

[6] Ibid., 20 (1904).

[7] Sciences, Arts, Nature, 6, 148.

[8] Revue des Sciences Photographiques, 1904, 257; 1905, 97. References are also given to the literature.

When I repeated Guébhard's experiments, using the pyro developer diluted to one-third, fifteen hours stand development of ordinary dry plates brought out reversed images similar in every respect to those obtained by Eder and by Liesegang as a result of adding substances which dissolve silver bromide to developers of normal concentration. If one takes a developer with only one-third the water in it that Guébhard recommends, a normal development is obtained with the same exposure. This is a further confirmation of what has been stated previously, that the reducing power of the solution must be decreased to cause the formation of a dichroic fog.

"When diluted sufficiently, any developer will fail to develop either the latent image or the chemical fog on an ordinary plate. Its only effect will be to reduce the whole of the silver bromide to colloidal silver. Thus a twenty- to thirty-hour treatment of normally exposed plates with a very dilute hydroquinone developer did not bring out a trace of an image, and the plates looked, after fixing, almost as though they consisted of unchanged silver bromide. This phenomenon was first described by Liesegang[1] who assumed that a thin film of metallic silver prevented the thiosulphate from fixing the plate. This hypothesis is incorrect because the apparently unfixed plates are made transparent by being bathed for a few minutes in a chromic acid solution. This proves that we were dealing with a very light modification of reduced silver and not with silver bromide at all. Under the microscope such films show only the uniform, round grain of the 'dichroic' fog and no trace of the ordinary fog-grain or even of unchanged silver bromide.

"With plates for transparencies, a fairly concentrated developer will cause the reversal of the image. Thus, with a *p*-amidophenol, soda developer, containing no sulphite, completely reversed images were obtained in two hours. In the same developer a highly-sensitive plate gave no sign

[1] Eder's Jahrbuch der Photographie, 15, 654 (1901).

of a reversal. The tendency to chemical development was so strong under these circumstances that even a long development brought out only a small amount of dichroic fog along with the normal image.

"Another case of pseudo-solarization, which has been known for a long time, depends on the use of thio-carbamides, and was described by Waterhouse[1] in 1891 in his paper entitled 'A New Method of Obtaining Direct Positives in the Camera.' A year later Waterhouse[2] attempted to give an explanation of the reversal caused by these substances and he described some electrochemical experiments in which these same compounds caused a reversal of the voltaic current. The action of the sulpho-ureas is however so similar to that of other substances which dissolve silver bromide that the same explanation must certainly apply throughout. In favor of this view are the later experiments of Waterhouse[3] and of Emerson Reynolds[4] in which it was shown that it is advisable to add ammonium bromide[5] to the developer in addition to the thiocarbamide.

"My own experiments confirmed completely the view, which I had previously expressed,[6] that the thiocarbamides act exactly like thiosulphate and other solvents[7] of silver bromide. The action of thiosinamine (allyl sulpho-urea) and still more that of thiocarbamide is so rapid that only very small amounts can be taken if one is to get a satisfactory reversal. Starting with 5 percent solutions, I added 0.5 cc. of the thiosinamine solution or 0.1 cc. of the thiocarbamide solution to 100 cc. of a hydroquinone-soda solution. Waterhouse recommended[8] especially the eikonogen developer

[1] Eder's Jahrbuch der Photographie, **5**, 283 (1891).

[2] Ibid., **6**, 170 (1892).

[3] Ibid., **16**, 482 (1902).

[4] Ibid., **17**, 460 (1903).

[5] Cf. Lüppo-Cramer, Photographische Probleme, 176 (1907).

[6] Phot. Correspondenz, **1905**, 162. I afterwards found that R. E. Liesegang had expressed the same view before me (Phot. Archiv, **1985**, 303).

[7] The solubilities of the silver halides in the thiocarbamides were determined quantitatively by Valenta (Phot Correspondenz, **1894**, 283).

[8] Eder's Jahrbuch der Photographie, **8**, 405 (1894).

and later the metol developer; but the nature of the development is of no importance. As I have said so often, the result depends entirely on the rate of development by the developer. In other respects the same points are important for a successful reversal, as with the reversals studied by Eder, Kogelmann, and Guébhard. The exposure must be just the right length and the amount of the substance dissolving silver bromide must depend on the relation between its own reaction velocity and that of the developer; a great deal depends also on the degree of ripening of the plate, on the time of development, etc., etc. Waterhouse himself mentions in his first paper that the composition of the solution must vary with the nature of the plate and with the object to be photographed. In fact he says at the end that the whole process is so new, so sensitive and involves such complicated chemical reactions that it will probably be some time before the process finds its way into practical use.

"When describing the experiments on pseudo-solarization, Liesegang[1] stated that the images that he obtained became very much darker when dried, and lighter when moistened again. I observed the same thing with plates developed in presence of thiocarbamide and this hangs together with the behavior of every fine-grained silver precipitate as is well known, for instance, in the case of silver chloride emulsions.[2]

"It may also be mentioned that the development with the thiocarbamides apparently never gives the lighter, distinctly 'dichroic' silver precipitates which are obtained with some of the other 'dichroic' methods of development. The precipitate often had such a uniform chocolate shade that one might easily think that another reaction had taken place. It is well known that the sulpho-ureas are easily saponified to carbon dioxide, hydrogen sulphide and ammonia.

[1] Phot. Archiv, 1895, 300.

[2] Cf. Lüppo-Cramer (Phot. Correspondenz, 1906, 492); also the important paper by Schaum and Schloemann [Zeit. wiss. Phot., 5, 109 (1907)], which appeared while this book was in the press.

Valenta[1] has also proved that the solution of silver chloride in thiosinamine is decomposed by alkalies with formation of silver sulphide. Bogisch[2] confirmed this for thiocarbamide. The solutions of silver bromide also undergo the same change. Nevertheless the action of chromic acid on the precipitate obtained by development in presence of thiocarbamides is in keeping with the view that, in presence of reducing agents, the deposit is at any rate chiefly silver. A microscopic examination shows a complete identity between the form of the grain in this case and in those in which other 'dichroic' developers were used. Also, the reversal with thiocarbamide occurs when one is using the acid iron developer, and the silver sulphide reaction cannot then occur.

"Among the reversals caused by substances which dissolve silver bromide, we must also include the normal development of plates exposed to the solarization point. This was done by Kogelmann,[3] using thiocarbamides, ammonium sulphocyanate, or thiosulphuric acid. The action is really not surprising, because at those points at which the greatest reduction would take place after a solarizing exposure, the reduction of the dissolved silver bromide would take place to the least extent. Since the silver reduced from the dissolved silver bromide has a much greater covering power than the other, the heaviest precipitates occur where there has been the greatest action due to light. I obtained only traces of the reversal of solarized images with thiocarbamide in the developer; but I got satisfactory reversals when I gave the plate a preliminary bath in a very dilute solution of thiocarbamide. Of course, with a reaction so complex and so dependent on a large number of variables, it is only occasionally that one gets a good picture. Since the Kogelmann solution of thiosulphuric acid is known to decompose very rapidly, it must be very much more difficult to get good results with it.

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[1] Eder's Jahrbuch der Photographie, 8, 413 (1894).

[2] Ibid, 8, 413 (1894).

[3] Phot. Mittheilungen, 31, 6 (1894).

In fact Kogelmann himself says that it is a difficult art to work successfully with thiosulphuric acid.

"Whether Kogelmann's development of solarized films with thiosulphuric acid corresponds to the similar experiments by Vidal[1] and to my explanation[2] of the latter depends chiefly on the exposure and on the time that the thiosulphate acts in Vidal's experiments. The brown color[3] of the image indicates that the change of the solarized latent image to a normal one is due at least in part to pseudo-solarization as a result of dissolved silver bromide.

"The cases of pseudo-solarization which have been described are all special cases of the phenomenon that ordinary development and the reduction of dissolved silver bromide are mutually antagonistic. We owe the first careful study of color fog as well as of many other points to R. E. Liesegang, and he explains[4] the tendency of the dichroic fog (red fog) to precipitate chiefly on the unexposed portions of the plate as follows:

'We shall see why the red modification of silver precipitates only on the unexposed portions and not on the exposed portions, if we recall that the red modification results from the reduction of a dissolved silver salt. On the exposed portions less silver bromide can dissolve in the small amount of thiosulphate because the silver bromide at those points has already been reduced to a certain extent to metallic (black) silver.'

"If we consider this explanation in connection with the obvious fact, also previously recognized by Liesegang,[5] that the fine-grained silver of the red fog has a very much greater covering power than the ordinary silver grain of a negative, and if we also keep in mind what I have previously pointed out, namely that silver germs, resulting from ex-

[1] Bull. Soc. Franç., 1898, 582.
[2] Lüppo-Cramer, Phot. Correspondenz, 1904, 123.
[3] Cf. Eder's Jahrbuch der Photographie, 16, 79 (1902).
[4] Phot. Archiv., 1895, 302.
[5] Ibid., 1895, 290.

posure to light, decrease the solubility of silver bromide, the phenomenon of pseudo-solarization becomes fairly intelligible.

"When comparing the fine-grained plates for transparencies with highly-sensitive plates, we must keep in mind the greater tendency of the latter to develop chemical fog and the readier solubility of the fine grains of the former. This difference comes out noticeably in those cases where colored fog is formed when there is no substance present which has a special tendency to dissolve silver bromide, with developers requiring no sulphite, such as *p*-amidophenol or pyrocatechuic acid. If one adds substances which dissolve silver bromide very rapidly, such as sulphocyanates, ammonia, etc., there is nothing like so marked a difference in the colored fog on the ordinary and the fine-grained plates.

"From the special case of stand development as it occurs in Guébhard's experiments, we deduce the important fact that when a developer of definite composition is diluted more and more, the power to produce chemical development decreases very much more rapidly than the power to reduce silver bromide to colloidal silver."

Lüppo-Cramer's idea is that the silver bromide dissolves and that metallic silver is then precipitated from the solution. This precipitation would naturally be heaviest at the points where there was the most silver bromide and could therefore cause a reversal. Lüppo-Cramer[1] has also shown that, with a metol-silver intensifier, silver is deposited very rapidly on fine-grained silver and much less rapidly on a silver with coarser grain.

Although recognizing the accuracy and ingenuity of Lüppo-Cramer's experiments, the work that we have done at Cornell leads us to suggest a somewhat different explanation, one that is really based on Lüppo-Cramer's own experiments.

In the previous paper,[2] it was suggested that the Waterhouse reversal, with thio-urea in the developer, might be the

[1] Eder's Jahrbuch der Photographie, 19, 411 (1905).
[2] Bancroft, Jour. Phys. Chem., 13, 459 (1909).

result of a displacement of the curve for composition and rate of development. On this hypothesis, the case would be precisely similar to the one which we meet when we change from a weak developer to a stronger one. Experiment has since shown that this hypothesis does not represent the facts. While the hypothesis does account for the production of a positive with a shorter exposure than is usually necessary, it postulates the possibility of developing a negative if the exposure is made shorter still. We have found that this negative cannot be realized and it is therefore necessary to account for the phenomenon in another way.

When a plate is immersed in a developer containing thio-urea, a negative first appears and afterwards a positive. After the plate has been fixed, it is usually possible to detect the two images on the plate by means of reflected light. The negative image is on the air side of the film while the more dense positive image is underneath it, and can be seen on the glass side of the film. It was found possible to duplicate these results by developing a weak negative in an ordinary developer and then immersing the plate in the developer containing the thio-urea. This proved that the negative image was the normal silver image usually obtained by development. To show that the presence of this silver image is not essential to the reversal, it was dissolved in a bath of acidified permanganate before the plate was placed in the developer containing thio-urea. The positive image, which was thus obtained, was of course somewhat better than that obtained under ordinary conditions because it was not blurred by the presence of a superposed silver negative. It was supposed that the positive image was silver sulphide; but analysis showed that it was almost entirely silver, so nearly so that the traces of silver sulphide could be attributed to side-reactions which had nothing to do with the theory of the phenomenon.

Since the positive image was essentially silver, it was clear that the sulphur in the thio-urea was of no importance as such and that some other property of the thio-urea was

the important one. Since there is a minimum exposure below which a given developer will not produce any image on a given plate in a given time, it was believed that the negative image might be suppressed entirely if the exposure were made sufficiently short, and that only the positive image would appear. Experiment confirmed this prediction completely. If the light had produced no change in the plate, no developer could have brought out an image, either positive or negative. Consequently we see that a so-called minimum exposure does change the plate although this change cannot be detected by means of the developer which contains no thio-urea. Since the developer containing thio-urea develops a positive image, it must develop the unexposed silver bromide more rapidly than that which has been exposed. A necessary corollary is that a developer which contains thio-urea will fog a plate which has not been exposed to the light. This was also confirmed experimentally. After we had reached this point, the rest was plain sailing. We know that ammonia dissolves silver bromide which has not been exposed to light more rapidly than silver bromide which has been exposed.[1] Thio-urea dissolves silver bromide.[2] Substances which dissolve silver bromide coarsen the grain and make the emulsion more sensitive.[3] The action of the thio-urea is therefore to make the unexposed silver bromide relatively more sensitive than the exposed bromide. If the exposure has been so short that neither the unexposed nor the exposed silver bromide will blacken in the developer containing no thio-urea and if the effect of the thio-urea is to carry the unexposed silver bromide over into a state where the developer can blacken it we shall get a positive as we actually do. If this explanation is the correct one, it ought to be possible to divide the process into two stages. If we bathe an exposed plate in a solution

[1] Englisch: Eder's Jahrbuch der Photographie, **19**, 363 (1905). Lüppo-Cramer: Ibid., **22**, 306 (1908).

[2] Reynolds: Jour. Chem. Soc., **53**, 861 (1888). Valenta: Monatsheft, **15**, 249 (1895).

[3] Lüppo-Cramer: Eder's Jahrbuch der Photographie, **21**, 367 (1907).

containing thio-urea alone, this should ripen the emulsion and we should then be able to develop the plate as a positive by washing it and then immersing it in an ordinary developer. This has actually been done. The Waterhouse thio-urea developer is therefore one having two entirely distinct functions. The thio-urea ripens the emulsion and the developer develops it. Unless the times of the two processes are adjusted very carefully, the result is bad, just as it is in a bath in which one tries to combine developing and fixing.[1] The more rational way under most circumstances is to use two baths and to have the process completely under control.

According to this point of view, sulpho-urea causes an increase in sensitiveness which is followed by chemical development, while Lüppo-Cramer believes that sulpho-urea dissolves silver bromide which is then changed to silver by so-called physical development. When the process proceeds in two stages, there is no sulpho-urea present when the developer is added. Consequently there can be no physical development unless we are going to call everything physical development, in which case we should have made no progress at all. I am quite prepared to admit that dichroic fog results to a large extent, perhaps entirely, from reduction of dissolved silver bromide to silver; but I do not admit that the formation of a dichroic fog is a necessary accompaniment of a reversal. Lüppo-Cramer himself admits that there is little or no dichroic fog when the reversal is brought about by means of thio-carbamide and our experiments confirm this. Lüppo-Cramer's explanation applies therefore to what is merely a fortuitous though frequent accompaniment of the reversal.

In the case of the Guébhard reversal the sensitizing agent is undoubtedly the sulphite.[2] It being an ineffective one, the developer has to be very dilute and the time of development has to be long. Kogelmann[3] found that a metol de-

[1] Baker: Phot. Jour., 28, 1 (1904).
[2] Cf. Liesegang: Arch. wiss. Phot., 2, 263 (1901).
[3] Eder's Handbuch der Photographie, 5th Ed., 3, I, 114 (1902).

veloper containing a good deal of ammonia gave reversals. Here the ammonia is the sensitizing agent.

In the previous paper,[1] it was pointed out that for a certain range of exposures, a strong developer will bring out a positive image and a weaker developer a negative. There are one or two interesting cases of this to which I wish to draw attention. Einsle[2] made a specialty of photographing the interiors of churches. Although the exposures varied from ten minutes to two hours and a half, he did not get a single poor negative. He attributed this result to his having used a slow developer, hydroquinone with very little alkali. The composition of the developer was: 40 grams sodium sulphate, 10 grams hydroquinone, 2 grams potash, 400 cc. water. Development lasted from fifteen minutes to an hour. While these plates were probably none of them over-exposed to the point of solarization, some of them had undoubtedly reached or were approaching the first zero state for the ordinary developer. By using a special developer, the exposure corresponded to the ascending part of the curve and good negatives resulted.

Eder[3] states that adding potassium bromide to a ferrous oxalate developer checks solarization with over-exposed plates while the addition of sodium thiosulphate increases solarization. The action of the bromide is exactly what one would expect because it slows up the developer. The action of the hyposulphite is not quite so simple. We are accustomed to look upon a hyposulphite solution merely as a solvent for silver bromide. As a matter of fact it is a reducing agent which may reduce silver bromide to metallic silver under favorable conditions. It may also act as a sensitizer to silver bromide and it can act on silver bromide which has been partially decomposed by light and can convert it into silver or a silver-rich substance by dissolving silver bromide out of it. This last property it shares with potassium cyanide,

[1] Bancroft: Jour. Phys. Chem., 13, 457 (1909).
[2] Eder's Jahrbuch der Photographie, 6, 111 (1892).
[3] Eder's Handbuch der Photographie, 5th Ed., 3, I, 114 (1902).

ammonia, etc, etc. Eder[1] says that "probably cyanide of potash is more effective than thiosulphate in splitting the sub-bromide into the soluble silver bromide and metal so that nitric acid dissolves what is left of the image;" and also that "what remains of the image after the preliminary fixing with ammonia can be developed physically very well, so that ammonia is not as effective as thiosulphate in decomposing the silver sub-bromide or, to put it in a better way, the substance forming the latent image. Instead it probably leaves a large part of the hypothetical subbromide intact and consequently this residual latent image withstands the action of concentrated nitric acid and fairly well.

"If we start with washed silver bromide collodion and expose the silver bromide to a strong light until it is blackened visibly, we shall find that ammonia, like thiosulphate precipitates so much metallic silver during the fixing process that this silver interferes with the phenomenon of development—physical development—and that only after this metallic silver has been removed by nitric acid (sp. gr. 1.20) does one see clearly the solarization effects always present in a silver bromide collodion plate which has been over-exposed so enormously."

Whether a hypo solution is to act chiefly as a solvent, as a reducing agent, as a sensitizer, or as a precipitant of silver, depends on the nature of the plate, the degree of exposure, the other things in the solution, the concentration of the hyposulphite and the time that the solution is allowed to act. As I hope to discuss this more in detail at some other time in another series of papers, I will content myself with having pointed out the intricacy of the problem. Since Eder did not have all the possibilities clearly in mind, it is not surprising that he should have written as follows:[2]

"At the point where solarization is just beginning, thiosulphate changes the latent image so that it then develops

[1] Cf. Jour. Phys. Chem., 13, 63 (1909).
[2] Ibid., 13, 62 (1909).

as clearly solarized, even at those places where otherwise a normal negative would have been obtained, or at most traces of solarization. When used for fixing the image before development, thiosulphate makes it possible to develop a solarized image as a normal picture or the normal latent image as a solarized picture. I was not successful, however, in determining any regularities, since the phenomena seemed to occur in a haphazard manner."

In the particular case under consideration, the hyposulphite probably acts as a reducing agent, since we know that it accelerates the ferrous oxalate developer if added in the proper proportions.[1]

There is now nothing obscure in Eder's remarks on the forcing back of the solarization limit by retarded development.[2]

"If one uses a very slow-acting developer, to which restrainers, especially potassium bromide, may be added if necessary, the limit of solarization can be forced back very much and the greatly over-exposed portions of the silver bromide plate may be developed as a normal negative even though they would solarize with the ordinary developers.

"If one develops such a plate with a pyrogallol-soda developer to which 1–10 percent of potassium bromide has been added, the solarization limit is forced back considerably. It is forced back still more by the mixture of edinol developer (1 : 25) with 1 percent solid acetone sulphite[3] as recommended by Precht, but the pyrogallol and potassium bromide gives a stronger negative with better gradations in the region of great over-exposures, well beyond the solarization limit. The same is true of many other developers.

"With respect to the rate of development of over-exposed plates, I mention merely that it is well known that many developers without alkali develop the latent image very slowly and that they act more energetically with increasing amounts of alkali."

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[1] Cf. Eder's Handbuch der Photographie, 5th Ed., 3, II, 465, 473 (1903).
[2] Cf. Jour. Phys. Chem., 13, 80 (1909).
[3] Phot. Correspondenz, 1902, 570.

The forcing back of the solarization limit by treatment with chromic acid or nitric acid before development is a simple matter theoretically. These acids dissolve silver readily, the silver-rich bromides less readily and the rate of action decreases as the silver content approaches that of the orthodox silver bromide. Consequently, nitric or chromic acid first eliminates the silver image of the second negative as has been previously pointed out.[1] It then dissolves silver to a certain extent from the silver-rich bromides, changing them into the form in which they develop as negatives. This method is applicable to almost any degree of over-exposure whereas it has been shown[2] that the method of retarded development gives positives when the over-exposure has been sufficiently great. This is exactly in line with the following statement by Eder[3] in regard to the matter.

"This treatment of solarized plates with chromic acid is more effective as a means of removing solarization effects than the mere variation (retarding) of the developer. This proves anew, what Lüppo-Cramer had already shown, that it would be false to consider solarization exclusively as a development phenomenon. As a matter of fact, by treatment with chromic acid, solarization can be eliminated over very wide ranges without changing the composition of the ordinary developer in the slightest. Furthermore, all the other methods, which I have recommended for eliminating solarization, work well and in a reliable manner."

Englisch[4] found that an over-exposed plate gave a positive on short development and a uniform blackening when developed for a longer time. If the plate is partially fixed before development, by soaking for five minutes in a 1 : 10 sodium thiosulphate solution, enough of the unexposed silver bromide dissolves to give a negative on long development. This change is a perfectly intelligible one. If silver

[1] Bancroft: Jour. Phys. Chem., 13, 461 (1909).
[2] Bancroft: Ibid., 13, 460 (1909).
[3] Jour. Phys. Chem., 13, 83 (1909).
[4] Eder's Jahrbuch der Photographie, 15, 608 (1901).

bromide is dissolved more rapidly where the change by the light has been the least, there will be more left where the effect of light has been the greatest. When the remaining silver bromide has eventually been blackened by the developer, the greatest blackening will be where there is the greatest residual amount of silver bromide, and we consequently get a negative.

Vidal's experiments[1] are apparently of the same type because he soaks his plate before development in a two percent solution of hyposulphite for two minutes. Though he does not say so, it is quite impossible that his plate should have been completely fixed under these conditions. Englisch used a 10 percent solution and soaked his plates for five minutes; but he speaks of his plates specifically as being only partially fixed.

At first sight, Kogelmann's experiments[2] with thiosulphuric acid and with sulpho-urea seem to come under this same head; but this is certainly not true as far as the experiments with sulpho-urea are concerned because the concentrations are so small that the amount of silver bromide actually dissolved by the sulpho-urea is negligible. The effect of the sulpho-urea must be the same as in the Waterhouse experiments and it must therefore increase the sensitiveness of the unexposed or partially decomposed silver bromide to the developer. In that case we should expect the greatest blackening where the action of light had been least, in other words, in the shadows. That would give a very dense plate consisting of two superposed positives, the blacker one coming from the sensitized silver bromide and the paler one from the latent image. Our experiments show that this is the normal result, though this seems not to have been recognized either by Kogelmann or by Lüppo-Cramer. It is probable that these gentlemen classed such plates among the "70 percent of failures." We have been rather more successful and we can

[1] Bull. Soc. Franç., 1898, 582.
[2] Phot. Mittheilungen, 31, 6 (1894).

duplicate our experiments indefinitely, getting positives or negatives as we please by varying the conditions of development.

As Lüppo-Cramer has pointed out, one has more control over the conditions if the process is carried out in the two stages of a preliminary bath in a sulpho-urea solution followed by development in a solution containing no sulpho-urea. If an old developer is used or a dilute one, there first develops an excellent positive which is the same positive that one would get if one were to omit all sulpho-urea. On further development the plate clouds and then a negative appears. This is the negative obtained by Kogelmann and by Lüppo-Cramer. It is rather a blurred negative because it is superposed with a positive. If the film is treated with a chromic acid solution, the negative image is destroyed before the positive image and we get back to a good positive if the attack is stopped at the right moment.

If the development of the plate is not stopped at the moment when the blurred negative is complete, the plate clouds again and we finally get a positive. If the developer is fresh and not too dilute, the intermediate stage of the negative is not detected. Kogelmann's negative image is therefore merely the result of retarded and incomplete development and does not represent anything more than a transitory stage. It seems probable that the appearance of the negative is primarily the result of a diffusion phenomenon, the sulpho-urea sensitizing the plate more rapidly at one point than at another. Why it should do this is of course an interesting problem but it does not come within the scope of this paper.

From the photographic point of view the Kogelmann negatives seem to be quite valueless because they are blurred. From the theoretical point of view, their value is not very great now that we know that they occur only as an intermediate step during development with exhausted or dilute developers. On the other hand, it would be of great interest if such an intermediate step could be brought to light in the Waterhouse process because that might give us extraordinarily

rapid plates. We are now making experiments along this line and we shall be able to report either positive or negative results in the next paper.

We can now take up Homolka's experiments.[1] Homolka[2] says:

"In several papers which have appeared in *Phot. Correspondenz* during the current year I have shown that one can develop the latent image on silver bromide gelatine by means of indoxyl or thioindoxyl and that the negative picture thus obtained is not homogeneous, but consists of a silver image and an indigo image." There is nothing surprising about this. When the silver bromide is reduced, the developer must be oxidized and the oxidation of the developer will be greatest at those points where the reduction of the silver bromide is greatest. In most cases the oxidation products of the developer are soluble. In the special case considered by Homolka, one of the oxidation products is blue (or red) and insoluble. Consequently we get a blue indigo image or a red thio-indigo image in contact with a silver image.

Homolka says further that "the two images can be separated without difficulty. If the developed and fixed plate is treated with a potassium cyanide solution, the silver image dissolves while the blue indigo image (or the red thio-indigo one) remains. However, if one treats the developed and fixed place with an alcoholic sodium hydrosulphite solution, the indigo picture dissolves as 'indigo-white' while the black silver image remains." There is nothing mysterious about this. The silver is removed by potassium cyanide which does not attack indigo, while sodium hydrosulphite reduces indigo without acting upon the silver. It would be easy enough to find other pairs of chemicals which would give similar results.

Instead of seeing that this result is the only one that could be expected under the circumstances, Homolka evolves a most ingenious theory. "From these facts we draw the

[1] Eder's Jahrbuch der Photographie, **21**, 58 (1907).

[2] Jour. Phys. Chem., **13**, 86 (1909).

conclusion that the substance of the latent image also is not homogeneous but must contain two constituents. One of these I consider a silver perbromide, perhaps $AgBr_2$; it can oxidize indoxyl to indigo and thus cause the indigo image. The other constituent is very probably a silver sub-bromide or the corresponding mixture of Ag + AgBr; under the action of indoxyl it is reduced to metallic silver, which presumably acts as a silver nucleus and causes the formation of the silver image."

Homolka overlooked the fact that if a sub-bromide of silver is reduced to metallic silver by the action of indoxyl, the indoxyl must be oxidized and consequently there is no reason to assume the existence of a perbromide in order to get the indoxyl oxidized.

Although the assumption of a perbromide is apparently unwarranted, Homolka describes two very interesting experiments which at first sight seem to confirm his view. "In the following way it proved possible to prepare the two constituents of the latent image separately by purely chemical methods without the intervention of light. If an unexposed dry plate is treated with very dilute bromine water, there is formed a latent perbromide image which develops in an indoxyl bath to a pure blue indigo image. On the other hand, if one treats an unexposed plate with a very dilute stannous chloride solution, there is formed a latent sub-bromide image which develops in the indoxyl bath to a black silver image."

It does not seem probable that this is a full statement of the facts. In the first place there is nothing to show what would have happened if there had been no silver bromide in the gelatine. If we assume, pending further investigation, that bromine compounds of gelatine play no part in the results, then treatment with a suitable stannous chloride solution must produce the same result as light and we must get both a silver image and an indigo image when we develop in an indoxyl bath. If the stannous chloride solution were a trifle too concentrated, it would reduce the silver bromide to a substance relatively low in bromine and there would then be

less indoxyl reduced relatively to the amount of silver produced. The blue image might then have been overlooked by one who was not especially on the watch for it. The experiment with bromine water becomes intelligible when we remember that bromine and many other substances increase the sensitiveness of silver bromide to the developer to such an extent that an unexposed plate fogs readily in the developer. Since the silver bromide is not reduced by the bromine water or the other substances as it is by light, there will be more indigo image formed relatively to the silver image than under normal conditions and we then face the possibility of the silver image having been overlooked.

As to the fogging effect of bromine water and other substances, I quote from Lüppo-Cramer.[1]

"Among the chemical reactions which point to a fundamental difference between chemical fog and latent image, the action of bromine water is of importance. In suitable concentration[2] it attacks the latent image on dry plates but leaves the chemical fog intact. With collodion plates neutral potassium bromide solution acts just as bromine water does on gelatine films, which is due to the greater 'protecting action' of gelatine previously mentioned. The action of bromine water is duplicated by that of a number of other substances,[3] such as potassium ferricyanide, permanganate, ferric chloride, and cupric chloride. All these substances act upon the latent image rather than on the chemical fog. In fact, in certain concentrations they add a not inconsiderable plus to the fog already present in ripened emulsions. Bromine water is able to produce fog when acting in concentrations which vary a good deal with the nature of the plate. Nitric acid, sulphuric acid, hydrochloric acid, and persulphate all fog highly sensitive dry plates completely while the latent image suffers very little by such treatment. Hydrogen peroxide

[1] Photographische Probleme, 131 (1907).

[2] The details of these experiments are given in Phot. Correspondenz, 1902, 634.

[3] Cf. Phot. Correspondenz, 1903, 224.

leaves a latent image completely intact even when it has produced the maximum amount of its well-known fogging action. . . . . .

"It is important to note that hydrogen peroxide, nitric acid, etc., only fog those plates which have a chemical fog[1] which accounts for the different way in which they act on different plates, as was pointed out also by Graetz in the case of hydrogen peroxide.[2] Since the peroxide also destroys the latent image and decreases the sensitiveness, we might assume that the action of radiation only takes place with highly sensitive plates, while with less ripened plates the chemical or oxidizing action predominates to such an extent that the radiation produces no perceptible effect.

"What however makes the action of these chemical reagents seem fundamentally different from that of light even though we should have to consider a radiation, is the fact that the light unquestionably causes a direct reduction which is quite out of the question with one class of fogging substances and is very improbable, to say the least, with another class, of which hydrogen peroxide in neutral solution is an especially good instance. At present we have practically no definite point of view as to the way in which fogging is caused by oxidizing agents, acids, salts of the metals, etc."

If the indoxyl developer has the power to reduce bromine compounds of gelatine in Homolka's experiments, it would not be necessary to assume that one of the images had been overlooked. This assumption would also be unnecessary in case Homolka did not wash out the bromine or the stannous chloride thoroughly. So far I have not been able to obtain copies of Homolka's original papers in *Photographische Cor-*

[1] Phot. Correspondenz, 1903, 227.

[2] The most remarkable instance is that of bromine water, the fogging effect of which has already been mentioned. Many kinds of plates are badly fogged by a brief immersion in very dilute bromine solution (5 cc. saturated bromine water to one liter of water). Many remain unchanged and some even lose some of their chemical fog. Similar irregularities were observed when sensitizing optically with some isocyanines. These are all cases which the orthodox chemistry of to-day fails utterly to handle.

respondenz and consequently I do not know definitely what precautions he did or did not take. It is quite certain, however, that there is an error somewhere in his results and we plan to repeat his experiments just as soon as we learn more details in regard to them.

Homolka's experiments in regard to solarization are also not conclusive.[1] "On a silver bromide gelatine dry plate which had been over-exposed to the point of solarization I was able to show that the indigo image, developed by means of indoxyl, is not solarized and that if the plate is first fixed and then developed physically, the resulting silver image is also not solarized. In fact both come out as normally graded negatives. From this the conclusion follows directly that the two latent images, the silver perbromide one and the silver sub-bromide one, were also not solarized. The amounts of the two effective constituents of the latent image—perbromide and sub-bromide—therefore increase continuously with increasing illumination and no reversal takes place. At first sight it appears paradoxical that the two latent images, when developed together chemically, should give a solarized picture. It becomes intelligible, however, if one reflects that the increase of perbromide and sub-bromide is necessarily accompanied by a decrease in the amount of the unchanged silver bromide—which last of course furnishes the material from which the silver image is developed. *I look upon this decrease in the supply of silver bromide as the cause of solarization.* With a certain degree of illumination there will be reached a certain equilibrium and the plate will perhaps show the maximum blackening if developed at the stage where there is exactly one molecule of silver sub-bromide (equal to one atom of silver nucleus) to one molecule of silver sub-bromide. If one exposes beyond this stage, there is an increase in the amount of silver perbromide and of silver sub-bromide (silver nucleus) while the amount of silver bromide decreases. If the plate is developed at this point, the silver

[1] Jour. Phys. Chem., 13, 87 (1909).

nucleus finds less silver bromide to influence than it did at an earlier stage and in consequence the density of the negative must decrease; in other words, there is a reversal of the image."

Homolka has assumed that the latent image was a normal one because he was able to develop a negative under special conditions, preliminary fixing followed by physical development. This is the more inexcusable because the change from positive to negative with changes in the developer or as a result of a preliminary treatment with reagents is perfectly familiar. In this particular case, the thiosulphate sets free more silver[1] from the parts which have received the most exposure and consequently more silver precipitates at those parts during physical development thus producing a negative. As Homolka does not state in his paper how he obtained his indigo negative on a solarized plate, we shall have to leave this point until the experiments have been repeated. There is no ground however for the assumption that Homolka's reasoning is better in the case where temporarily we cannot check him than it is in the cases where we can check him.

The explanation of the solarization as due to the decrease in the amount of unchanged silver bromide is pretty unsatisfactory from any point of view and it involves the explicit assumption that the unchanged silver bromide "of course furnishes the material from which the silver image is developed." This assumption may be true, though I doubt it; but there is no of course about it and it should not be used as a starting-point in an argument until it has been justified to some extent. This is the more necessary because Englisch[2] states explicitly that only the silver bromide which has been exposed can be developed.

Stenger[3] has noticed that thin films reverse more quickly than thick ones. Other things being equal, this would of course be the case because the light would have more chance to act on the silver bromide.

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[1] Bancroft: Jour. Phys. Chem., 13, 548 (1909).

[2] Eder's Jahrbuch der Photographie, 15, 605 (1901).

[3] Ibid., 22, 384 (1908).

Englisch[1] claimed that solarization was not a continuous process; but his arguments seemed to have been disposed of by Vojtech[2] who showed that Englisch's results were vitiated by the unsteadiness of the burning magnesium ribbon which he used as a source of light.

Blanc[3] has published a paper on sensitive reversible plates for the production of reversed positives in the camera and I quote an abstract of it,[4] with a few verbal changes.

"The author says he has lately obtained a gelatino-bromide emulsion which is of interest because its action is just the reverse of an ordinary emulsion. Plates coated with it blacken completely without exposure to light, and, if exposed, the action of the developer diminishes in proportion to the length or intensity of the exposure. He at once took advantage of this curious property to obtain some copies by contact in a pressure frame and some transparencies in the camera, which, although weak, were well defined. They could be intensified by ordinary methods. With short exposures of a second in the camera, these plates gave a very feeble negative, and the film blackened all over if the development were pushed.

"An interesting experiment was to cut a plate in two, then to expose one-half for about a minute near a window, keeping the other in the dark. On developing them side by side in the same developer, the exposed plate began to darken slightly while the other remained white, but as the development went on, the latter darkened and became quite black, while the former did not change further, so that after fixing, the two portions of the plate showed a striking contrast when laid upon white paper, the one being black and the other a grayish white.

"The author's explanation is that the production of an emulsion of definite character is never homogeneous, it always

[1] Zeit. wiss. Photographie, 1, 364 (1904).
[2] Eder's Jahrbuch der Photographie, 19, 386 (1905).
[3] Bull. Soc. Franç. (2), 17, 256 (1901).
[4] Phot. Jour., 25, 319 (1901).

contains more or less of others in different states. He considers that, in his reversing plates, there is a minimum quantity of normal emulsion which, under the action of light, produced the graying of the piece exposed, and to this small quantity of normal emulsion may be attributed the weak negative image obtained in the camera with short exposure. And if, by under-exposure and prolonged development of normal plates, fog is produced, this is probably due to a small quantity of reversing emulsion formed at the same time as the normal emulsion.

"The author's reversing emulsion was obtained by carrying on the ripening of the normal emulsion until it showed a colorless image of the sun instead of a blue one. It would seem therefore that a certain degree of ripening may produce effects due to a prolonged action of light on ordinary sensitive plates. In the latter the formation of the latent image is attributed to a partial dissociation of silver bromide, the entire film containing this salt in the natural state; in the reversing plates, on the contrary, the entire coating would have undergone a commencement of dissociation and the latent image would be constituted by the renewal, by the light, of the silver bromide in its natural state."

What Blanc has done is to ripen his emulsion to such an extent that the silver bromide has been reduced either by the gelatine or by other substances in the emulsion to the stage corresponding to the zero state. Exactly the same effect could have been obtained by fogging with light or in a number of other ways. By retarded development it would probably have been possible to have developed a negative instead of a positive, though this cannot be proved now.

This case is fundamentally different from and must not be confused with one cited by Sterry which I shall now discuss. Sterry[1] published a short note on the reversal of the photographic image by means of under-exposure which seems to me of fundamental importance though I have not been able to find any further reference to the matter.

[1] Phot. Jour., 27, 290 (1903).

"Some forms of chemical fog in an emulsion are discharged by weak light, the greatest protective result being found with an exposure about equal to that which first causes reduction by development in the usual way. It is therefore possible to obtain a direct positive with an exposure about thirty to forty times less than that required to obtain a negative. A plate (preferably chloride) must be chosen which cannot be used in the ordinary way without a restrainer in the developer. It is then found only necessary to develop a short exposure without bromide to obtain a positive and a longer exposure with bromide (to obtain) a negative.[1] As the two images overlap, it has not been found possible so far to obtain the high lights without any fog. Similar results were obtained by General Waterhouse[2] by the addition of thio-carbamide to the developer, and by the writer[3] by means of auxiliary exposure, but in the present case the result is obtained solely by development without bromide."

In the discussion that followed, "Mr. Sterry added that he had brought an example for those present to see. The upper plate, which had a variety of exposures, was cut in halves; the one part was developed in a solution containing bromide and made an ordinary negative, and the other without bromide, which showed as an ordinary negative at one end and as a positive at the other. Below that, he had made a positive from an autotype set up of test negatives from which a direct positive from the positive was obtained with a very short exposure. At present there had been no application of this, but General Waterhouse had said that, if done effectually, direct positives might be useful in astronomical work. In this case, however, he found that only special plates acted satisfactorily. Perhaps a study of emulsions might reveal something regarding the separation of the two images, and they might eventually obtain enormous rapidity."

[1] The examples shown were made upon a 'Gaslight' lantern plate with a paramidophenol developer, using a double quantity of potassium carbonate.

[2] Jour. Phot. Soc. India, 3, 160 (1890); 4, 21 (1891).

[3] Brit. Jour Phot., 1893, 686.

We have succeeded in duplicating these experiments of Sterry's using ordinary bromide plates. Of course, if we have a plate which fogs in the developer and if light prevents the formation of fog, we shall necessarily get a positive on development, which is just what happens. A statement of what seem to be the experimental facts is not an explanation, though it may be the first step towards one. At present we do not know at all why light should check the formation of chemical fog under any conditions and it is possible that we may have to take up the whole question of chemical fog in detail before we can find an answer to the problem. For the moment we are busying ourselves with questions of manipulative detail. Later, we hope to discuss the theory of the process.

Carey Lea[1] has discussed some interesting analogies between the action of light and the action of sodium hypophosphite. Since the results appear to involve a reversal by sodium hypophosphite, I quote at length:

"I next pass to the consideration of the identity existing between the photo-salts and the material of the latent image. Before entering, however, on that matter, it is necessary to describe a reaction leading to the formation of these photo-salts, somewhat differing from the reactions already mentioned, and which has important bearing on the subject.

"The remarkable action which an alkaline hypophosphite exerts on salts of copper was described many years ago by M. Würtz. Its action on silver salts, though there is no parallelism between the two, has enabled me to find a key to some of the great difficulties of the latent image.

"A dilute solution of sodium hypophosphite, if poured over a mass of chloride, bromide or iodide of silver formed in the absence of light, produces no visible effect, but has the property of bringing those substances into the condition in which they exist in the latent image. Applied in strong solution and with the aid of heat, it produces brown-purple

[1] Am. Jour. Sci. [3], 33, 482 (1887).

photochloride, bromide and iodide of silver. I will here briefly describe the first of these compounds in order to continue the series of photochlorides, and then pass to the consideration of the latent image.

Photochloride of Silver by Sodium Hypophosphite

"Silver chloride, freshly precipitated with excess of HCl and well washed, placed in a flask with a strong solution of sodium hypophosphite and heat applied begins to darken before the boiling point is reached. Actual boiling for ten or fifteen minutes gives a deep chocolate color. This product well washed and freed from traces of metallic silver by cautious boiling with very dilute nitric acid has a pink, red or brown color varying in intensity according to the length of the action. Sometimes a lavender shade is produced, and this is more apt to be the case when the silver chloride has been precipitated with excess of silver nitrate instead of excess of HCl.

"Silver determinations of two specimens of the purified product were made, indicating the presence in one specimen of 1.77 percent of subchloride, in the other of 3.53.

"By the continued action of heat for many hours a complete reduction to metallic silver takes place.

"Photochloride obtained in this way has generally a brown or dull purple color. Boiled with nitric acid it is apt to break up in as many minutes as some other forms would require hours for decomposition, yielding white chloride, while the nitric acid takes up small quantities of silver.

Identity of Photo-salts with the Material of the Latent Image

"It is proposed here to show:

"1st. That in the entire absence of light, sodium hypophosphite is able to affect a sensitive film of silver haloid exactly in the same way as does light, producing a result equivalent to a latent image formed by light and capable of development in the same way as an actual impression of light.

"2nd. That these two effects, the impression produced by hypophosphites and that by light, comport themselves to reagents exactly the same way and seem every way identical.

"3rd. That the image produced by hypophosphite on silver chloride always gives rise to a positive development, but on silver bromide may give rise either to a direct or to a reverse image, both of these effects corresponding exactly with those of light. More than this, sodium hypophosphite may be made to reverse the image produced by light on silver bromide and conversely light may be made to reverse the action of hypophosphite. So exact a correspondence in these remarkable properties can scarcely be fortuitous.

I

"A silver haloid formed in the absence of light and subjected to the action of sodium hypophosphite gives rise to the gradual formation of sub-salt, which combines with the normal salt in the manner described in the previous part of this paper. This action of the hypophosphite closely corresponds with that of light. In its initial stages it is invisible, but can be brought out in both cases by development.

"If we form a film of chloride, bromide or iodide of silver and with a glass rod dipped in solution of hypophosphite make marks upon it, these marks can with the utmost ease be developed in precisely the same way as an image produced by exposure to light.

"A very simple mode of operating consists in imbibing photographic paper with a solution of alkaline haloid, drying, applying a silver solution and then thoroughly washing, all of course with careful exclusion of active light. If the silver solution is acidulated with nitric acid, a drop to the ounce, the result is brighter, but this is not important. In any case the washing must be thorough.

"Marks made on this paper can be developed with the oxalate developer with the utmost facility. If a strong solution of hypophosphite is applied cold, it may be washed off at the end of a minute, but a stronger impression is obtained

by allowing it to wait half an hour before developing. Or the action may be accelerated and increased in strength by laying the freshly marked paper on a hot surface, or better, by steaming it, before applying the developer. A convenient mode of steaming is to lay two pieces of glass on a small water bath kept boiling, with a space between them. Over this space the paper is rested for two or three minutes. Paper prepared with a solution of KCl, KBr, or KI, dried and floated on acidulated solution of silver nitrate and well washed, if marked with strong solution of hypophosphite and steamed for two or three minutes, will develop the marks as black as ink on a white ground. The use of heat simply gives a blacker development, but a very vigorous image may be got without.

"(A similar result may be obtained by substituting for the hypophosphite a dilute solution of potash and an oxidizable organic substance. With milk sugar the action is very energetic and heat is quite superfluous.)

"Both these are the initial steps of reactions which, when prolonged, result in the visible formation of the colored photo-salts. It is a matter of interest that sodium hypophosphite, which produces the above-described effects, has no developing power whatever.

II

"The two impressions, that formed by light and that by hypophosphite, are similarly affected by reagents.

"As an example of this identity of effect produced on the two impressions, I first take the action of nitric acid.

"Chloride, bromide and iodide papers were exposed to moderate diffuse light under a screen with openings, for a proper time to form a latent image, the chloride and bromide for four or five seconds, the iodide for twenty or twenty-five. They were then cut into halves and one-half of each was soaked in strong nitric acid for five minutes. These halves were then washed for some hours and were developed along with the halves not so treated. Result was, latent image on silver chloride almost if not quite uninjured; on silver

bromide, somewhat affected but still strong; on silver iodide entirely destroyed.

"Similar portions of the same papers were then marked with hypophosphite and were cut into halves and one-half was subjected to the action of nitric acid in exactly the same way as the previous. The result was exactly as before. The hypophosphite marks on the half of the chloride paper that had been treated with acid came out in development as vigorously as on the half that had not been treated. The bromide paper showed the marks weakened by the acid but still strong; on the iodide not a trace appeared. In all respects the result was the same: what the one resisted the other resisted, what destroyed the one destroyed the other.

"Another confirmation is presented by the action of the alkaline haloids upon the latent image.

"The latent images produced by light on chloride, bromide and iodide of silver were all treated with cold and moderately strong solutions of potassic chloride, bromide and iodide for half an hour, and were then subjected to development. It was found that all three silver salts bore the action of potassic chloride and bromide fairly well, the images were somewhat weakened but strong developments were obtained without difficulty. But when potassic iodide was applied the latent image was totally destroyed.

"The visible effect of the alkaline haloids on the photo-salts exactly corresponds with their action on the latent image. Potassic chloride and bromide, applied in moderately strong solution and cold have little effect, but potassic iodide quickly destroys them.

"Therefore the action as well of nitric acid as of KCl, KBr and KI is exactly the same on the latent image impressed by light on AgCl, AgBr and AgI as it is on the corresponding photo-salts.

III

"The impressions produced by alkaline hypophosphite upon silver chloride always give rise to direct images, darker

than the ground on which they are formed. The same substance produces an impression on silver bromide which may by development produce either a direct or a reverse image. So that there is a perfect parallelism with the action of light.

"The reverse action of light, sometimes called solarization, shows itself as follows. A film of bromide being exposed to light, part covered by an opaque screen, the exposed portion receives an impression capable of development, and this impression grows in strength to a certain point, then recedes and reaches a condition in which it is less susceptible of development than before exposure. All bromide films, even unexposed to light, will darken in a developing solution in time. The portion that under the action of light has reached the reverse stage resists the reducing action of the developer better than that which was not exposed at all, and consequently appears after development as light on a dark ground and is therefore a reverse image. As to the cause of this action we are as yet wholly in the dark. If the continued effect of light was simply to restore the affected part to its original state we might attempt an explanation by affirming that the continued action of light undid its own work. But the fact of the resistance to reduction being greater than before exposure shows that some as yet unknown action of light is in play. The reverse action cannot be due to oxidation as has been suggested, because hypophosphite reverses and certainly cannot oxidize.

"The reversing action of light on silver bromide finds its counterpart in the action of sodium hypophosphite.

"If we take bromide paper (it is immaterial whether in making it the bromide or the silver solution be applied first, but for these experiments on the reversal of the image it is essential that a pure neutral silver solution be employed and that after the second solution has been applied the paper should be thoroughly washed, all the operations being of course performed by inactive light:) If we take such paper and make marks on it with a strong solution of hypophosphite, and then throw the paper into potassio-ferrous oxalate,

we shall get a direct development; the marks will be stronger than the ground. If now we continually weaken the hypophosphite solution, we shall presently reach a point at which these marks are in development almost wholly indistinguishable from the ground on which they were made. But continuing the dilution still further we presently reach a point at which the marks reappear, but this time reversely, as lighter marks on a darker ground. This result is obtained with about a 2 percent solution; the first-mentioned effect comes with a solution of 25 or 30 percent. So that according as we use the hypophosphite solution stronger or weaker we obtain exactly opposite effects. Here the parallelism is striking but not perfect, at least it remains to be explained why the action in the two cases proceeds in a reverse order. All the other reactions show a perfect identity.

"Time will also sometimes produce the same effect as dilution. Paper marked and put away for 24 or 48 hours, giving at first a direct image, may after that time give a reverse one. This effect is extremely uncertain and I think, exceptional. I have kept very many pieces for periods from a few hours to several weeks, which first and last gave direct images only; a few became reversed. But the experiment itself, the opposite effect of strong and weak solutions, is liable to no such uncertainty.

"Again, we may make light and hypophosphite interact and each reverse the other's action.

"To make hypophosphite reverse the action of light, I take a piece of silver bromide paper, expose it to the action of diffuse daylight for a few seconds, then taking it to the dark room, make marks upon it with a glass rod dipped in solution of hypophosphite. On developing with potassio-ferrous oxalate the marks appear lighter than the ground. Or what is perhaps more striking, we take two pieces of such paper, retain one in the dark room and expose the other from 5 to 20 seconds to diffuse light, then make marks on both with a glass rod dipped in strong solution of hypophosphite, and then, after allowing a few minutes for the hypophosphite

to act, place them both in a solution of potassio-ferrous oxalate. The marks will develop, in the one case, as dark on a light ground, in the other (that exposed to daylight) as light on a dark ground.

"We have here made the hypophosphite imitate the action of light: it has reversed the image in the same way as would result from a prolonged exposure to light. It will next be shown that light may be made to imitate the action of hypophosphite and reverse the effect already produced by that or other reducing agent.

"If we take the red or purple silver bromide, preparing it with exclusion of light and the same precaution as in the case of a dry plate and extend it over paper (it is best, though not essential, to mix it with a little gelatine to enable it to retain its hold on the paper in the subsequent treatment), dry it and expose it to light under a screen such as a piece of opaque stiff pasteboard with openings cut in it, then apply potassio-ferrous oxalate, we shall obtain a very remarkable effect: all the parts exposed to light take a reversed development and appear as lighter spaces on a dark ground. And this goes so far that we may expose till we get a visible and quite strong image, darker than the ground and yet in development this darker portion will come out lighter than the ground. Indeed I have one specimen which shows almost white figures on an intensely black ground. Before development these light figures were brown, by exposure to light, on a rose-purple ground. I have seen few more curious results than this.

"From the foregoing it follows that red bromide, notwithstanding its intense coloration, is in the same condition respecting light as normal silver bromide that has received an impression of light so strong that any further influence of light would cause reverse action, only that a vastly larger proportion of its molecules are affected. In the case of the latent image formed by light on normal bromide it would seem that the particles affected, although numerous enough to serve as a basis of development, are still too few and too scattered to be visible or affect the color. The photobromide on the

contrary has its mass made up of them. Then if exposed to light, the light carries them a stage farther—brings them to the reverse or 'solarized' condition and the parts affected by light develop less strongly than those not exposed.

"So light can act the part of hypophosphite and hypophosphite that of light, interchangeably; each can produce a direct action, each a reverse and each can reverse the other.

"It then appears that in all the numerous ways in which it is possible to compare the photo-salts with the material of the latent images they are found to be identical. The proofs based on development generally, and especially on the reversal of the latent image seem very strong and these receive additional support from the exact identity of reactions shown by the photo-salts and by the material of the latent image.

"The question of the identity of the photo-salts with the products of light on the silver haloids might perhaps be left with some confidence to the cumulative proofs here offered. But I hope to be prepared to give in the next number of this Journal additional evidence from a new direction."

The extraordinary thing about Carey Lea's results is that he gets a dark image on a light ground with his concentrated sodium hypophosphite solution and a light image on a dark ground with the dilute solution. If we are to consider the sodium hypophosphite solution as equivalent to light, we are getting a negative with an intense light (concentrated solution) and a positive with a weak light (dilute solution), which is just the reverse of what we should expect. At first I thought that the negative with the concentrated solution corresponded to the second negative, in which case there should be another negative with a more dilute solution than any Carey Lea had used. This proved not to be the case. It was then found that one could get either a negative or a positive depending on the length of time that a concentrated sodium hypophosphite solution is allowed to act. The reason for this is that sodium hypophosphite can act both as a reducing agent and as a solvent for silver bromide. If a plate is long enough in a concentrated solution there is practically

nothing left to develop. If it is only immersed for a relatively short time, the reducing action of the hypophosphite is the more important and the treated portion develops dark. At the time that we made these experiments, we had not worked out the sensitizing action of sulpho-urea and consequently no experiments were made to determine to what extent, if any, sodium hypophosphite would sensitize unexposed silver bromide apart from a straight reduction.

In the next paper on solarization, I expect to discuss the methods of obtaining positives with relatively short exposures. The principles involved have now been brought out clearly, but there are some points in regard to the application of them which seem to me to be of interest.

The general results of this paper may be summed up as follows:

1. The Waterhouse reversal is due to a sensitizing of the emulsion by thio-urea. Better control is obtained by giving a preliminary bath in a thio-urea solution and then developing with an ordinary developer.

2. The Guébhard reversal is similar in principle to the Waterhouse reversal. The difference between the two processes is due to the relative inefficiency of sodium sulphite as a sensitizer.

3. Some special cases of retarded development have been discussed in detail.

4. Englisch's and Vidal's development of an over-exposed plate as a negative by means of a preliminary partial fixing has been shown to be a necessary consequence of the selective solvent action of sodium thiosulphate.

5. Kogelmann's work on developing negatives from over-exposed plates after treatment with thio-urea has been repeated and it has been shown that negatives are obtained only when the developer is old or dilute and even then only when development is not carried too far.

6. Homolka's experiments with indoxyl have been discussed in detail and the fallacies in his reasoning have been pointed out.

7. Blanc's reversing emulsions are emulsions which have been fogged to the zero state.

8. Sterry's experiments on the effect of light in discharging fog from chloride plates have been duplicated with bromide plates. The phenomenon is to be studied more in detail.

9. Carey Lea's apparent reversals with dilute sodium hypophosphite and not with concentrated sodium hypophosphite have been shown to be due to the fact that sodium hypophosphite may act both as a reducing agent and as a solvent for silver bromide.

10. It has been shown that thin films should reverse more rapidly than films provided all other conditions are alike; but it is not claimed that this is necessarily, or even usually, the case.

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OPTICAL ACTIVITY AND THE PRODUCT OF ASYMMETRY.

BY J. WALLACE WALKER.

In a recent communication[1] Bose and Willers have attempted to show that there is a possibility of determining a constant of optical activity for each atom or radical attached to an asymmetric carbon atom. The constant for a given radical is of such a nature that it will express the optical effect of such atom or radical no matter what the compound be into which it is introduced, and from these constants they endeavor to show that the molecular rotation of any compound containing these radicals may be calculated by Crum Brown's equation for the product of asymmetry, *viz.*, $M[\alpha] = (C_1 - C_2)(C_1 - C_3)(C_1 - C_4)(C_2 - C_3)(C_2 - C_4)(C_3 - C_4)$, where C_1, C_2, C_3 and C_4 are the activity constants of the four atoms or radicals. The authors, after discussing the various aspects of the case, decide that it is better to choose the activity of pure liquids instead of solutions for comparison and they of course limit themselves to such as are likely to be free, or nearly so, from polymerization. For this reason they have selected the esters of the following acids bromopropionic, chloropropionic, valeric, lactic, glyceric, bromosuccinic, chlorosuccinic, malic, methoxypropionic, ethoxypropionic, methoxysuccinic, and ethoxysuccinic acids. In all, 42 substances are thus available and these contain 17 different radicals, for which they deduce the constants:

Radical	Constant	Radical	Constant
—H	12	—$CH_2.COOC_3H_7$	24.0
—CH_3	0	—$CH_2.COOC_4H_9$	24.2
—C_2H_5	0.053	—Cl	9.0
—$COOCH_3$	9.5	—Br	8.75
—$COOC_2H_5$	9.34	—OH	11.81
—$COOC_3H_7$	9.21	—$CH_2.OH$	20.35
—$COOC_4H_9$	9.13	—OCH_3	12.7
—$CH_2.COOCH_3$	22.2	—OC_2H_5	12.8
—$CH_2.COOC_2H_5$	23.0	—	—

[1] Zeit. phys. Chem., **65**, 702 (1909).

Using these values, they proceed to calculate the molecular rotations of the various 42 substances and find on the whole a fairly close agreement with the experimental results. The higher limit of the ratio $\frac{\text{calculated}}{\text{observed}}$ is 1.466 and its lower limit is 0.507. Those who are familiar with the difficulties and uncertainties attending the preparation of pure optically active substances, free from any admixture of racemoid, will best appreciate whether these limits are too wide for much reliance to be placed on the generalization which the authors attempt to deduce. If one cannot rely on obtaining a sample of a compound containing less than 50 percent of racemoid, as the above values would indicate, this detracts very seriously from the value of measurements of this physical property of substances, and this feeling has doubtless been responsible for the recent partial cessation of activity on the part of investigators in this field. It is worthy of remark however that the greatest deviations quoted above occur in the case of the glyceric esters, which, on account of the number of hydroxyl groups that they contain, might fairly be expected to show considerable polymerization of their molecules and therefore to be less comparable with the other liquids.

This subject engaged the attention of the writer some years ago and an endeavor was then made to deduce such a series of constants but it was discarded as fruitless for a reason which will appear in the sequel. Meantime it may be of interest to note a few of the values which led to the hope that such an expectation might be realized:

Radical	Constant	Radical	Constant
—OH	110	$—CH_2.COOCH_3$	61
—H	100	$—COOC_2H_5$	60
$—CH_2OH$	92	$—CH_2.COOC_2H_5$	56
$—CH_3$	90	$—C_2H_5$	52
$—COOCH_3$	65	—Cl	49

The values calculated for the molecular rotations of the following substances by means of these constants are given

in the second column of the following table, the observed values in the third. The fourth column contains the ratio $\frac{\text{calculated}}{\text{observed}}$ and the fifth column the corresponding ratio for Bose and Willer's values.

Substance	M[α]	Calculated × 10⁻⁵.	Calculated / Observed	
			Walker	Bose and Willers
Methyl lactate	796	788	0.990	1.280
Ethyl lactate	1216	1200	0.987	0.963
Methyl chloropropionate	2888	2927	1.013	1.170
Ethyl chloropropionate	2576	2760	1.071	1.006
Methyl malate	1115	1203	1.130	1.329
Ethyl malate	2025	1901	0.939	0.970
Methyl glycerate	576	612	1.063	1.466
Ethyl glycerate	1230	922	0.750	0.791
Methyl valerate	1950	2074	1.064	0.875
Ethyl valerate	1750	1751	1.001	1.002

It is evident from this table that the ratios $\frac{\text{calculated}}{\text{observed}}$, obtained by means of these constants, show in the main a slightly closer approach to unity than those from Bose and Willers' numbers. In one important respect they have an advantage over the latter, in that they show a diminution of rotation on ascending the series of valeric esters in conformity with observed facts, whereas their numbers show an increase. When however the rotations of the chlorosuccinic esters were calculated the divergence was much greater, the values obtained being for methyl chlorosuccinate 5346 instead of M[α] = 7650 and for ethyl chlorosuccinate 2765 instead of M[α] = 5730. In the latter case the discrepancy is over 50 percent and that in the wrong direction from what a knowledge of the experimental conditions would lead us to anticipate, since the observed value may easily be too low through racemization having occurred during the action of phosphorus pentachloride on the malic ester. It is far less

likely that it is too high. This result indicated that it was necessary either to reject the values selected for the constants altogether and to look for another series of numbers—a task which seemed endless—or to devise a crucial method of determining if it may not be impossible to assign rotation equivalents to all radicals from which the molecular rotations of the substances containing them may be calculated by Crum Brown's equation. The method finally evolved was as follows:

It is possible to select *eight* distinct optically active substances, whose molecular rotations we may call $M[\alpha]_1$, $M[\alpha]_2$, * * * * * $M[\alpha]_8$, all possessing *one* common radical, whose rotation equivalent is C_1, and whose other radicals may be chosen from a group of *six* with the rotation equivalents C_2, C_3 * * * C_7. Now, forming the products of asymmetry for each pair of substances which have *three* radicals in common, equating to their molecular rotations and dividing the one equation by the other, we obtain:
for the radicals

C_1, C_2, C_3, C_4 $$M[\alpha]_1 = (C_1 - C_2)(C_1 - C_3)(C_1 - C_4)(C_2 - C_3)(C_2 - C_4)(C_3 - C_4)$$

C_1, C_2, C_3, C_5 $$M[\alpha]_2 = (C_1 - C_2)(C_1 - C_3)(C_1 - C_5)(C_2 - C_3)(C_2 - C_5)(C_3 - C_5)$$

hence $$\frac{M[\alpha]_1}{M[\alpha]_2} = \frac{(C_1 - C_4)(C_2 - C_4)(C_3 - C_4)}{(C_1 - C_5)(C_2 - C_5)(C_3 - C_5)} \quad \ldots\ldots (1)$$

C_1, C_2, C_6, C_4
C_1, C_2, C_6, C_5 Similarly $$\frac{M[\alpha]_3}{M[\alpha]_4} = \frac{(C_1 - C_4)(C_2 - C_4)(C_6 - C_4)}{(C_1 - C_5)(C_2 - C_5)(C_6 - C_5)} \quad \ldots\ldots (2)$$

C_1, C_7, C_3, C_4
C_1, C_7, C_3, C_5 Similarly $$\frac{M[\alpha]_5}{M[\alpha]_6} = \frac{(C_1 - C_4)(C_7 - C_4)(C_3 - C_4)}{(C_1 - C_5)(C_7 - C_5)(C_3 - C_5)} \quad \ldots\ldots (3)$$

C_1, C_7, C_6, C_4
C_1, C_7, C_6, C_5 Similarly $$\frac{M[\alpha]_7}{M[\alpha]_8} = \frac{(C_1 - C_4)(C_7 - C_4)(C_6 - C_4)}{(C_1 - C_5)(C_7 - C_5)(C_6 - C_5)} \quad \ldots\ldots (4)$$

Now, if we further divide equation (1) by equation (2) and equation (3) by equation (4), we find that, if the radicals possess such a property as that of an 'optical activity con-

stant,' a very simple relationship must hold between the rotations of the substances selected, namely

$$\frac{M[\alpha]_1}{M[\alpha]_2} / \frac{M[\alpha]_3}{M[\alpha]_4} = \frac{(C_3 - C_4)}{(C_3 - C_5)} / \frac{(C_6 - C_4)}{(C_6 - C_5)} = \frac{M[\alpha]_5}{M[\alpha]_6} / \frac{M[\alpha]_7}{M[\alpha]_8}.$$

Among the very extensive series of known optically active liquids, however, it was found that there were none which exactly fulfilled the above requirement, *viz.*, *eight* substances with only *seven* radicals, one of which is common to all. The group which approached most closely to it consisted of the methyl and ethyl esters of lactic, mandelic, chloropropionic and phenyl chloroacetic acids, but the methyl mandelate, with its melting point of 55°, had only been examined by Walden[1] in carbon bisulphide and in acetone solutions. As its rotation in the one solvent is just about double of that in the other, it is obvious that neither could be assumed to represent the activity of the pure liquid substance. Further, since the property of optical activity has in general a large temperature coefficient and the other substances had all been measured at 20°, it was necessary either to re-examine all at a temperature above 55° or to obtain methyl mandelate as a greatly supercooled liquid. I had already prepared the lactates and the chloropropionates from them,[2] but as the method employed, namely, the action of alkyl iodides on silver lactate, has been shown to give a product contaminated by alkyl oxypropionate[3] and as my results for the chloropropionates and bromopropionates differed very widely from those obtained by Walden,[4] it was considered advisable to prepare them all again with the utmost care and examine them over a range of temperature. The results obtained at 20° and at 70° are contained in the following table, the others will be found in detail at the end of this communication.

[1] Zeit. phys. Chem., **17**, 707 (1895).
[2] Jour. Chem. Soc., **67**, 914 (1895).
[3] Purdie and Irvine, Ibid., **75**, 484 (1899).
[4] Ber. chem. Ges. Berlin, **28**, 1293 (1895).

	M[α] at 20°	M[α] at 70°	
Methyl lactate	796	966	$M[\alpha]_1$
Ethyl lactate	1216	1434	$M[\alpha]_2$
Methyl mandelate	27590	23820	$M[\alpha]_3$
Ethyl mandelate	22570	19710	$M[\alpha]_4$
Methyl chloropropionate	2888	2524	$M[\alpha]_5$
Ethyl chloropropionate	2576	2207	$M[\alpha]_6$
Methyl phenylchloroacetate	7002	5978	$M[\alpha]_7$
Ethyl phenylchloroacetate	6622	5571	$M[\alpha]_8$

Substituting the values at 20° in the equation to be tested, we find for the numerator

$$\frac{797}{1216} \Big/ \frac{2759}{2257} = 0.535$$

and for the denominator

$$\frac{2888}{2576} \Big/ \frac{7002}{6622} = 1.060.$$

Instead of being equal to the numerator, the denominator has just double its value. Of course, the degree of molecular association is not likely to be exactly the same in the whole of the eight substances although, all being esters, it is improbable that any of them are highly polymerized. The effect of rise of temperature is, however, to reduce association and, therefore, their rotations at 70° have also been compared. Substituting these values, we find

$$\frac{966}{1434} \Big/ \frac{2382}{1971} = 0.557$$

and

$$\frac{2524}{2207} \Big/ \frac{5978}{5571} = 1.066.$$

The improvement is less than 4 percent. Consequently, if we may accept these values as being even approximately correct, and there seems no reason to suppose that there has been extensive racemization in one member more than in the others, it follows that this investigation must be regarded

as disproving the existence of a fixed coefficient of optical activity for each radical in the sense expressed by Crum Brown's equation, as applied by Bose and Willers.

EXPERIMENTAL

Part I, with Dr. Samuel Smiles

The esters of mandelic and phenylchloroacetic acid were prepared by us some years ago, using every precaution to insure purity and avoid racemization. The mandelic acid, obtained from amygdalin, was repeatedly recrystallized until it melted sharply at 132.2°. Its specific rotation in 2 percent aqueous solution at 17° was found to be $[\alpha]_D$ = — 154.2°. The esters were made from it by means of the silver salt and alkyl halides, and they were very carefully crystallized from a mixture of benzene and light petroleum until they also showed very sharp melting points. After their physical constants had been determined, they were then transformed into the corresponding phenylchloroacetic esters by the action of phosphorus pentachloride upon their solutions in dry chloroform. The phenylchloroacetic esters were finally purified by fractional distillation under reduced pressure. Their densities were very carefully determined and their rotations in the liquid condition even at temperatures much below the points of solidification of the mandelates. These results are tabulated below.

MANDELATES

	Methyl ester, M. P. 54.3°		Ethyl ester, M. P. 30°	
Temperature	Density	M[α]	Density	M[α]
10°	1.1848	—28630°	1.1383	—23300°
20	1.1756	27950	1.1290	22570
30	1.1660	26760	1.1200	21920
40	1.1568	25960	1.1105	21300
50	1.1472	25170	1.1015	20750
60	1.1380	24450	1.0920	20220
70	1.1284	23820	1.0830	19710

n-Propyl ester, M. P. 24°			*n*-Butyl ester, M. P. 31°	
Temperature	Density	[M]α	Density	M[α]
10°	1.1100	—21130°	1.0800	—
20	1.1005	20540	1.0720	—21990°
30	1.0915	19980	1.0632	20380
40	1.0827	19400	1.0545	19780
50	1.0740	18860	1.0460	19220
60	1.0645	18320	1.0370	18740
70	1.0556	17770	1.0283	—

PHENYLCHLOROACETATES

Methyl ester, B. P. 124° at 8 mm			Ethyl ester, 133° at 12 mm	
Temperature	Density	M[α]	Density	M[α]
10°	1.2175	+7417°	1.1678	+6818°
20	1.2080	7002	1.1580	6622
30	1.1980	6596	1.1490	6416
40	1.1886	6301	1.1393	6200
50	1.1790	6135	1.1297	5993
60	1.1692	6033	1.1202	5777
70	1.1600	5978	1.1110	5571

n-Propyl ester, B. P. 140° at 19 mm			*n*-Butyl ester, 163–4° at 20 mm	
Temperature	Density	M[α]	Density	M[α]
10°	1.1390	+5905°	1.1130	+6791°
20	1.1290	5736	1.1040	6591
30	1.1195	5565	1.0950	6387
40	1.1100	5368	1.0860	6174
50	1.1010	5210	1.0773	5978
60	1.0913	5041	1.0680	5770
70	1.0817	4863	1.0595	5556

Several of these substances had already been examined by Walden[1]. His observations made at 20° are subjoined for comparison.

[1] Zeit. phys. Chem., **17**, 705 (1895)

	Density	M[α]
Ethyl mandelate	1.1270	—22161°
Methyl phenylchloroacetate	1.2087	+19843°
Ethyl phenylchloroacetate	1.1594	+ 4999°
n-Propyl phenylchloroacetate	1.1278	+ 5087°

The agreement is far from satisfactory, except possibly in the case of ethyl mandelate. For methyl phenylchloroacetate, Walden gives a value 2.83 times greater than ours, but his value places that substance in a separate category from the other members of the same series, which is unlikely, whereas our determinations show a similar progressive change from member to member in the series of phenylchloroacetates as in the series of mandelates.

Part II, with Mary Violette Dover

The esters of lactic, chloropropionic and brompropionic acids have already been described by one of us[1] but it has since been shown by Purdie and his pupils that the silver salt method which was employed in making the lactic esters, is liable to yield a material contaminated with alkyl oxypropionic esters. The latter are highly optically active substances, and are difficult to eliminate by the only method of purification available in this instance, namely, fractional distillation, consequently we decided, in preparing the lactic esters, to employ the ordinary method of esterification by means of alcohol and sulphuric acid. The salts of active lactic acids, from which the esters were made, was obtained by the method of Purdie and Walker.[2] As larger quantities of material were available than formerly, greater care in purification was possible. The results obtained were as follows:

[1] Walker, Jour. Chem. Soc., **67**, 914 (1895).
[2] Jour. Chem. Soc., **67**, 616 (1895).

METHYL ESTERS

Lactate B. P. 60–61° at 35 mm			Chloropropionate 49–50° at 35 mm		Bromopropionate 61–62° at 36 mm	
Temperature	Density	M[α]	Density	M[α]	Density	M[α]
10°	1.1005	—762°	1.1950	+2973°	1.5130	+8245°
20	1.0895	796	1.1815	2888	1.4975	7973
30	1.0785	836	1.1680	2806	1.4825	7666
40	1.0670	871	1.1550	2731	1.4675	7391
50	1.0560	904	1.1410	2663	1.4525	7140
60	1.0450	936	1.1280	2590	1.4375	6872
70	1.0335	966	1.1140	2524	1.4225	6610

ETHYL ESTERS

Lactate B. P. 68–69° at 37 mm			Chloropropionate 59–60° at 37 mm		Bromopropionate 70–71° at 36 mm	
Temperature	Density	M[α]	Density	M[α]	Density	M[α]
10°	1.0405	—1160°	1.1010	+2654°	1.4035	+6500°
20	1.0300	1216	1.0890	2576	1.3895	6240
30	1.0190	1264	1.0770	2503	1.3757	5998
40	1.0080	1310	1.0650	2422	1.3615	5756
50	0.9975	1353	1.0530	2298	1.3475	5530
60	0.9856	1395	1.0415	2274	1.3335	5311
70	0.9751	1434	1.0300	2207	1.3195	5090

The results of this careful examination vary somewhat, although not greatly, from those previously found. To enable a direct comparison to be made, we have obtained the values of M[α] for each ester at the same temperatures as those at which the former observations were made by interpolation or slight exterpolation.

METHYL ESTERS

	Lactate	Chloropropionate	Bromopropionate
Former preparation	—1154°	+3287°	+7133°
Present preparation	— 778°	+3023°	+8023°

ETHYL ESTERS

Former preparation	—1713°	+2714°	+5702°
Present preparation	—1209°	+2634°	+6272°

The molecular rotations of the lactates and chloropropionates are found to be somewhat lower, and those of the bromopropionates somewhat higher than the values given formerly.

The lack of concord between the results obtained by different investigators in these series of substances may be mainly due to the comparative ease with which racemization occurs in replacing the hydroxyl group by chlorine, and may be considered to detract from the reliability of the conclusion drawn in the theoretical part of this communication. Further, the lowest members of any homologous series are those which show greatest divergences from the generalizations which have been drawn regarding other physical constants, for example, the boiling points. For this reason, it has been considered advisable to select other substances for an examination in which it is hoped that both of these disadvantages may be avoided. The series selected is that of the esters of the asymmetrical aliphatic acids and the work has been for some time in progress.

NEW BOOKS

A Text-Book of Experimental Chemistry. *For Students of General Inorganic Chemistry. By Edwin Lee. 14 × 21 cm; pp. xv + 433. Philadelphia: P. Blakiston's Son and Co., 1908.*—In the preface the author says:

"No hesitancy has been manifested in introducing physico-chemical generalizations wherever they seemed necessary to rational correlation and explanation of facts. The importance of these generalizations in connection with the teaching of general chemistry is now generally recognized, yet the writer confesses that he knows of no text-book on 'experimental chemistry' which has been brought abreast of the times by appropriating and incorporating the results of the labors of the physical chemist. It may be true that physical chemistry cannot and should not be taught in the first year of chemistry, but in the opinion of the author and at least one other, 'many of these generalizations which have been brought in by this new physical chemistry, can and should be introduced into general chemistry.' The author would not leave the impression that the older generalizations and methods of developing the subject have been abandoned; on the contrary, they have been retained and an effort has been made to rationalize them by supplementing them with more recent data taken from the domain of physical chemistry. The book represents, therefore, an effort to fuse modern views and recent advances with those older views which have stood the test, and to explain chemical phenomena in a manner that is in accord with modern chemical thought.

"The rôle of energy in chemical reaction has been given unusual prominence. The elements of thermochemistry have been presented. More space has been allotted to 'solutions,' 'the ion theory,' 'chemical equilibrium' and the 'mass law' than is usually given in books of this character. It is believed, however, that the results obtained warrant this. A brief comprehensive statement of the historical development of the 'electrolytic dissociation theory' has been given that the student may become familiar with the story of the gradual development of at least one chemical theory. The author has observed that students take a keen delight in stating just how much was contributed to the development of a chemical theory by this or that chemist. With a similar purpose in view, the writer has quoted references *verbatim*, rather than record the gist of them."

In the introductory portion of the book the chapters are entitled: fundamental concepts; characteristics of physical and chemical changes; elementary substances, mixtures and compounds; note on the energetics of chemistry; science, its methods of development—classification; quantitative relationships, laws and chemical equivalents; outlines, theories, formulae, valencies, equations, units; oxygen; hydrogen; water; solutions; acids, bases and salts; chemical equilibrium, reversible reactions, mass law, dissociation; note on the modern theory of solution.

This is an interesting book and could be read with profit by every teacher of introductory chemistry. Whether it will meet the needs of Freshmen satisfactorily is an entirely different matter. For the people who are taking a course

in chemistry as part of a general education, the more physical chemistry they get the better. In fact, one could defend the thesis, that they might be given a great deal of physical chemistry without any chemistry in the old-fashioned sense of the word at all. To the chemist it seems a horrible thing that a man should not know that salt is sodium chloride and that he should not be able to write reactions; but with each one of us it is merely a question where our knowledge breaks down and where we deal solely with words. In order to avoid any possible hard feeling, I will take myself as a painful example. Every other year I talk to my students about Jellett's experiments on the distribution of an acid between quinine and codeine. I don't know what the formula of quinine is or of codeine and, what is more, I don't care. For the purpose in hand, it is only necessary to know that they act as bases. Of course, some one may say that it involves some knowledge of chemistry to know what a base is. Ordinarily it does; but I don't know that that is essential. We could get along for a while with a statement that an acid tasted sour and that a base turned a solution of what we call phenolphthaleine red. This gives me another illustration. Every chemist at some time in his life has used phenolphthaleine as an indicator, but we are still squabbling as to what happens.

Nearly everybody knows that sugar dissolves in water and the knowledge which they might get in regard to solution is not dependent in any way on whether they know the structure formula for cane sugar. In some respects the non-chemists hit the nail on the head pretty well. In my experience they usually say that the sugar melts in the water which is a fact that most physical chemists still fail to grasp in its entirety.

The reviewer believes firmly that it would be a very good thing if the chemistry taught in the high school consisted of a maximum of physical chemistry and a minimum of straight chemistry so-called. The course could be labeled "The Chemistry of Every-Day Life" if that would eliminate difficulties.

While the reviewer sympathizes with the author's point of view and while he might perhaps be even more extreme under certain circumstances, he considers the question still open as to what amount of physical chemistry should be taught to Freshmen who are planning to become chemists. There is the time limit to be considered and also the fact that the study of qualitative analysis has to be taken up in the next term. The question then is whether the student can get a sufficient grounding in chemical facts if he has also to absorb a lot of physical chemistry, valuable though the latter is. It is quite possible that it is better for the student to take his medicine in two doses and to avoid mixed drinks.

As the reviewer has said on other occasions, it is only by seeing how the thing works in practice that we can tell what is the best way to teach chemistry to a Freshman—and even then we shall probably not agree. Books of this type are extremely valuable as showing the different tests which are being carried out.

The reviewer was grieved to find the saying that "the exception proves the rule" given a scientific standing, p. 40, and backed by the authority of Richards. Both Richards and the author, of course, know what the freshmen will not know; that, as usually applied, this is a hopeless corruption and that 'prove'

originally had the significance of 'test.' The thing is quite on a par with the alleged medical advice to "stuff a cold and starve a fever."

Wilder D. Bancroft

A Laboratory Outline of General Chemistry. *By Alexander Smith. Third Edition. Revised in Collaboration with William J. Hale. 12 × 19 cm; pp. vii + 136. New York: The Century Co., 1907.*—In the preface the authors say:

"When quantitative experiments were first used in elementary chemistry it was hoped that they would also assist in developing an abiding realization of the quantitativeness of all chemical phenomena and, as a consequence, make all the thought and work of the student more rigorous. In the experience of the authors, however, quantitative experiments of the usual kind fail to accomplish this important result. Students who have performed such experiments still add a test-tube full of sulphuric acid to a liquid known to contain only a trace of a compound of lead, and still think less than a dozen bubbles of hydrogen sulphide sufficient to precipitate the lead from 10 cc. of approximately normal lead nitrate solution. They attempt to make potassium chlorate without considering that a few bubbles of chlorine (perhaps liberally mixed with air) will not saturate three grams of potassium hydroxide, or they take too much water and then, not having considered the solubility and, therefore, not knowing what is wrong, throw away the product and lose valuable time by starting entirely *ab initio*. The failures which result from this lack of a sense of quantity are innumerable, and the discouragement often a serious hindrance to ultimate success. The fault, of course, is in the instruction, and the remedy lies in exercises and questions devised to cultivate *this* missing sense. It is to meet this situation that the tables of solubilities have been introduced and have been referred to frequently. With the same object, the tables of degrees of ionization have been utilized and the varying degrees of activity of acids have been observed and measured. Still further to cultivate rational experimentation, the solutions on the side-shelf should be approximately normal (or in simple multiples or submultiples of this concentration), and the student may then be led to note the concentrations and, in many experiments, to take suitable quantities accordingly. The importance of this point of view indicated in the foregoing can hardly be overestimated. Genuine success in business or in the professions, and often the mere making of a livelihood, depend so largely on ability to reason quantitatively that practice in this kind of reasoning is of inestimable value in education. If, on the contrary, the work in chemistry is purely haphazard in this respect, the study of the science may easily be a positive detriment rather than a benefit, and that whether the student ultimately makes direct use of his knowledge of the science or not.

"If it appears that these changes have made the work more difficult, it must be remembered that valuable knowledge can be obtained only by effort, and that the value of the knowledge is in proportion to the effort, provided the latter is directed rationally along instructive lines. Easy chemistry must be superficial and empirical, in proportion ito its simplicity. It is easy to perform experiments mechanically; it is necessarily more difficult to interpret the results and extract all that they can teach."

If the use of this book in the laboratory will cause the student to think, the book will mark the beginning of a new epoch. Even if it should not do as much as that, it is important to cultivate the sense of quantity. The wide scope of the experiments may be inferred from the fact that the authors have included a modification of Buchholz's experiments with tin, stannous chloride and water, p. 119. *Wilder D. Bancroft*

Introduction a l' Étude de l' Électricité statique et de Magnétisme. *By E. Bichat and R. Blondlot. Deuxième èdition, entièrement refondue. 14 × 23 cm; pp. viii + 188. Paris: Gauthier-Villars, 1907. Price: paper, 5 francs.*—In the first part, on static electricity, the chapters are entitled: fundamental phenomena; action of two electrified masses, one on the other; definitions; theorem of Gauss; potential; experimental study of the electric field; tubes of force and lines of force; propositions in regard to conductors; electrical diagrams; electrical equilibrium; capacity; condensers; work and electrical energy; derived units and the C. G. S. system; electroscopes and electrometers; applications of electrometers; electrical machines; specific inductive power; electric spark; decay of an electrical charge. In the part on magnetism, less than forty pages, the chapters are entitled: magnets and magnetic field; laws of magnetic repulsions and attractions; terrestrial magnetism. The book is avowedly elementary, and is intended to meet the requirements for entering the *École Polytechnique*. On p. 13 the authors give a reproduction of a cut from Coulomb's original memoir. *Wilder D. Bancroft*

Le Principe de la Conservation de l'Assise et ses Applications. *By Georges Matisse. 16 × 25 cm; pp. 65. Paris: A. Hermann, 1907. Price: paper, 2.50 francs.*—Instead of considerinng the different forms of energy as the products of the potential into the capacity, the author prefers to use the word *assise* instead of *capacité*. As capacity factors for different forms of energy, he takes the quantity of electricity, the entropy, the volume, the distance, the quantity of matter which is measured by the mass.

The author's law of the constancy of the capacity factors rests on the following facts.

1. In an isolated system the total quantity of electricity remains constant.
2. In a reversible transformation constituting a closed cycle, the change of the entropy is zero.
3. The mass of a system in an enclosed space remains constant no matter what physical or chemical changes take place.
4. If a system is enclosed in a rigid envelope, the volume remains constant no matter what physical or chemical changes take place.
5. The rectilinear distance between two fixed points remains constant even though the relative positions of movable points along the line may change.

The "law" can be formulated in the following way: "Physical and chemical changes do not create electricity, space (cubical or linear), entropy, or matter." Comment would seem to be unnecessary. *Wilder D. Bancroft*

SOME ZINC ALLOYS

BY B. E. CURRY

Antimony-Zinc

Considerable work has been done on the antimony-zinc series of alloys but even the latest efforts leave much to be desired in accuracy and completeness.

A number of definite compounds have been credited to this series. Cooke[1] was the first to work with these alloys. He isolated compounds to which he gave the formulas Zn_3Sb_2 and ZnSb. Herschkowitsch[2] made a series of electromotive force determinations from which he deduced the existence of the compound $ZnSb_2$. The freezing point curve was determined by Rolland-Gosselin.[3] This curve consisted of four branches and indicated two compounds of uncertain composition. Heycock and Neville[4] determined only a small portion of the freezing point curve and on this account their data are not of value here.

More recently Mönkemeyer[5] has redetermined the freezing point curve and has worked over the series microscopically. This freezing point curve consists of four branches with two maxima and three eutectics. The maxima appear at 35 and 45 percent zinc while the eutectics appear at 22, 37 and 97.5 percent zinc. The diagram is shown in Fig. 1. The four phases separating from the melt are pure antimony ZnSb, Zn_3Sb_2 and pure zinc. The inversion point noted in pure zinc at 321° introduces a fifth phase which would seem to indicate an allotropic form of zinc. If not a second form of zinc, the data are incomplete. Also the fact that the inversion tem-

[1] Am. Jour. Sci. (2), **18**, 229 (1854); **20**, 222 (1855); **30**, 194 (1860). Phil. Mag. [4], **49**, 405 (1860).

[2] Zeit. phys. Chem., **27**, 123 (1888).

[3] Bull. Soc. d'Encouragement (5), **1**, 1301, 1310 (1896). Cf. Gautier: Contributions à l'étude des alliages, 101, 110 (1901).

[4] Jour. Chem. Soc., **71**, 394, 402 (1897).

[5] Zeit. anorg. Chemie, **43**, 182 (1905).

perature varies over a range of 30° indicates inaccuracies or error due to unstable conditions. Theoretically across the Zn_3Sb_2 + Zn field this inversion temperature must be constant.

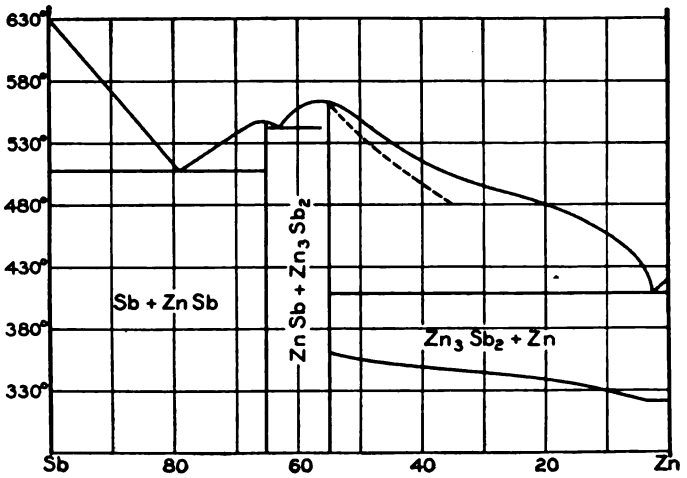

Fig. 1

Independently Zemczuznyj[1] duplicated the work of Mönkemeyer. He found similar freezing point data except that no maximum appeared at 35 percent zinc and therefore no minimum between this and the 45 percent composition. Also his work proved that the inversion or modification which Mönkemeyer found in zinc at about 320° was due to a change in the Zn_3Sb_2 compound and not to a change in the zinc. The diagram is shown in Fig. 2. This work also leaves the Zn_3Sb_2 inversion point determinations incomplete because the line KM representing the inversion temperature has no logical ending. Theoretically this line should have a constant temperature across the Zn_3Sb_2 field and should end somewhere beyond the Zn_3Sb_2 composition. The cause of the wide range of the inversion temperature is evidently due to supercooling.

In this work I have redetermined the melting point curve. In the main it is coincident with the curve obtained

[1] Zeit. anorg. Chem., 49, 384 (1906).

by Zemczuznyj. The observations were made on heating curves and the difficulties which are met with on cooling curves were thus eliminated. As a further precaution the observations were made on ingots that had been annealed and which had therefore reached equilibrium. On this

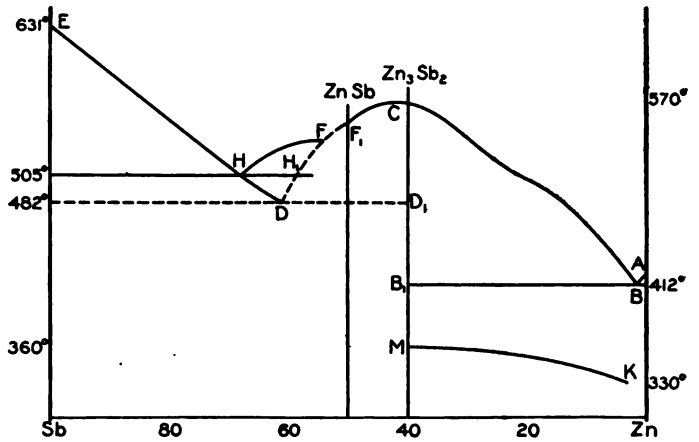

Fig. 2

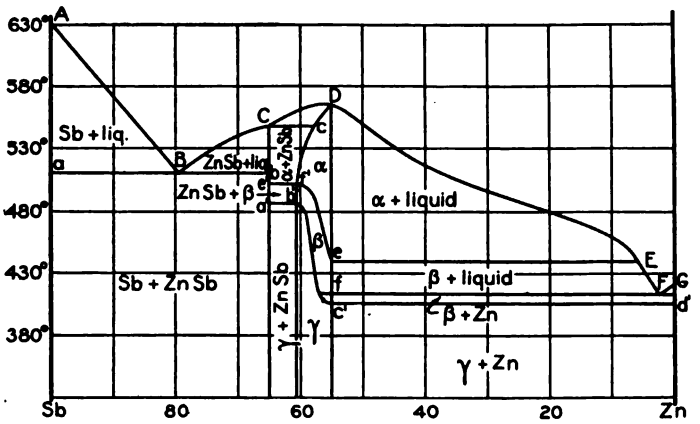

Fig. 3

account the heat changes which Zemczuznyj found over the ZnSb + Sb field did not appear in these observations. The heating curve data follow in Table I. These data are represented graphically in Fig. 3. In the melting point curve,

which consists of five branches, only one maximum and two eutectics appear, one at 22 percent and the other at 97.5 percent zinc. The series forms a melting point curve with five branches. It appears, however, as will be explained later, that only four phases actually separate from the melt. Along the branch AB pure antimony separates from the melt; along BC the stable phase is ZnSb; along CDE the solid solution α is in equilibrium with the melt. The β phase separates from the melt along the new branch EF; along FG the stable phase is pure zinc.

TABLE I

Percent zinc	Liquidus	Solidus	Inversion		
100	[illegible]	—	—	—	—
97.5	411	[illegible]	[illegible]	—	—
[illegible]	[illegible]	[illegible]	[illegible]	—	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	—	—	—
[illegible]	[illegible]	[illegible]	—	—	—
[illegible]	[illegible]	[illegible]	—	—	—
[illegible]	[illegible]	[illegible]	—	—	—
[illegible]	[illegible]	[illegible]	—	—	—
[illegible]	[illegible]	[illegible]	—	—	—
[illegible]	[illegible]	[illegible]	—	—	—
	[illegible]	[illegible]	—	—	—
[illegible]	[illegible]	[illegible]	—	—	—
	[illegible]	[illegible]	—	—	—

[illegible]

liquidus and at the eutectic temperature 505°. The heat evolution which Zemczuznyj noted below the eutectic on cooling curves across this range does not appear in the heating curves. The 35 percent zinc alloy shows but one heat absorption on the heating curve and that at 546°, the melting point. The alloys containing from 35–45 percent zinc show four breaks in the heating curves. These represent two inversion temperatures, the solidus and the liquidus. The horizontal portion of the solidus represents the temperature at which the phase changes into ZnSb and vice versa. On cooling the melted alloys, the partial inversion of α into ZnSb may not occur until many degrees below the solidus. This was noted by Zemczuznyj. The fact that the horizontal lines e′f′ and a′b′ can not be followed beyond 42 percent zinc shows something concerning the width of the α, β and γ fields. These inversions do not appear on cooling curves and have been overlooked until this time. The lines F′c and b′c′ lie between single phase fields and therefore are not limited to a constant temperature.

Heating curves on alloys containing from 45–95 percent zinc show four heat absorptions. These represent two inversion points, the solidus and the liquidus. The first inversion point occurs at a temperature of 405° along the line c′d′ and 6° below the solidus. This represents the inversion of the γ phase into β. The solidus occurs at 411° along the line fF. The second inversion temperature occurs at 437° along the line eE. At this temperature β changes over into α. The change which comes just below the solidus or eutectic is likely to be obscured by the eutectic heat absorption. On cooling, this change may not appear until as much as 75° below the stable temperature. On reheating to the eutectic and recooling, the inversion again takes place far below where it appears on the heating curve. No evidence of the change of α into β appears on the cooling curve. On this account α crystals continue to separate from the melt below 437° unless crystals of β be added for nuclei. Along the branch EF or from 95–97.5 percent zinc β crystals separate

from the melt. Over this range three breaks occur in the heating curves of the inversion temperature of γ into β, the solidus and the liquidus. From 97.5 percent zinc to pure zinc the heating curves show breaks only at the solidus and liquidus. The mass of eutectic masks the heat absorption of the inversion of the small quality of γ into β.

The thermal data show that the compound ZnSb does not combine with more antimony, and form a solid solution. The eutectic is readily traced from pure antimony to the compound ZnSb. The same is true of the eutectic formed between β and pure zinc. The thermal data taken below the CD portion of the CDE branch show that the phase which separates here is a solid solution rather than a definite compound.

This series of alloys shows the inadequacy of cooling curve determinations. The freezing point curve for this series may be determined very accurately by this method. The same may be said for the solidus. On the other hand when one solid phase should change into another, it does not change. As a result the temperature at which the change does occur may be many degrees below where it should appear. In other instances the change does not appear at all on the cooling curve. Neither Mönkemeyer nor Zemczuznyj noted the inversion points in the alloys with 35–45 percent zinc. If equilibrium were established readily, breaks would have appeared in the cooling curve. In the 90 percent zinc alloy they found an inversion point at about 330°. This should have appeared at 406° or 76° higher. In one of these instances we have seen an error of 76° and the other the non-appearance of the second phase. At present we have no reason to doubt the appearance of inversion points on heating curves. While we know that super-cooling is very common, the phenomenon of superheating is quite rare.

The inversion points found across the concentration between 35 and 45 percent zinc, as has been stated, do not appear on any of the cooling curves. They do appear, however, on heating curves. In making the determinations

the rise in temperature was made at the rate of about 4° per minute. Under these conditions the breaks in the heating curve appear sharply and definitely. The inversion temperature below the eutectic with 45–100 percent zinc is best located by heating at a rate of only about 2 or 3° per minute. Otherwise the heat absorption at the eutectic is likely to obscure the other. When an ingot is heated from room temperature there is no evidence of any heat absorption below 405°, thus showing that the inversion located there by Mönkemeyer and Zemczuznyj was inaccurate. When this same ingot is cooled from the eutectic or from above 405° the cooling curve shows a definite break, depending on the composition and rate of cooling, from 20–80° below the stable temperature. This series of alloys affords excellent examples of what errors the investigator of alloys is likely to make if the data are collected by means of cooling curves alone.

Microscopically the equilibrium diagram for the antimony-zinc alloys consists of six phases. Two of the phases are the pure components, antimony and zinc. All alloys, containing less than 35 percent of zinc, contain crystals of ZnSb. When these alloys are etched with alcoholic ferric chloride in hydrochloric acid, the antimony crystals etch white and the ZnSb crystals appear as the dark phase. Across this range, the amount of the antimony crystals decreases as the composition ZnSb is approached. The alloy containing 35 percent zinc etches dark with the above solution and shows only faint traces of the white antimony crystals. This alloy is homogeneous when chill-cast. This structure is not changed by annealing. The crystals appear as large plates. These alloys have no inversion points and the only effect of annealing is to increase the size of the crystals. These alloys come within the ZnSb + Sb field in Fig. 3. As the zinc content is further increased, a new white phase appears. The 36.9 percent zinc alloy contains large amounts of a second phase which etches white. This phase is only slightly attacked by the dilute acids and is much less soluble than the phases with which it comes into equilibrium. As the zinc

content is further increased to 39.5 or 40 percent, the amount of the new phase increases and the ZnSb crystals diminish in amount and disappear at about 40 percent. Alloys with a zinc content of 40 to 45 percent are homogeneous when chill-cast and when annealed. When these alloys crystallize from the melt, the α phase appears first; at lower temperature under equilibrium conditions, the α phase breaks down into the β and then the γ modifications. Both the microscopical and thermal data disprove the formation of the compound Zn_3Sb_2. So far as the microscopical data are concerned, these three phases have no distinct differences. Annealing the ingots at different temperatures does not change the crystalline structure. Neither do any of the etching solutions employed differentiate between these three phases. Except for the thermal data there is no way of differentiating one from the other. When the α phase is cooled, the cooling curve does not indicate the appearance of the other phases at the lower temperature. In the irregular fields designated α, β, and γ these phases appear as large, bright crystals. Between these fields and the ZnSb composition there is a mixture of ZnSb crystals with α, β, or γ, depending upon the equilibrium temperature. Across these narrow fields the crystalline structure appears the same independent of the annealing temperature. The α, β, and γ fields have approximately the same maximum width. The α phase is instable below 437° and the β phase breaks down at 405°. The γ phase does not come in contact with the melt and therefore is not represented on the freezing point curve.

All alloys with more than 45 percent zinc are inhomogeneous under all conditions. Below 405° and under equilibrium conditions, these alloys are composed of crystals of γ and zinc. Between 405° and 411°, β is in equilibrium with zinc. The crystalline structure over this range is doubtless very similar to that below 405°. Above 411°, α and β are in equilibrium with melt as shown in Fig. 3.

As completed, the equilibrium diagram consists of six phases—pure antimony, pure zinc, the compound ZnSb and

three series of solid solutions α, β, and γ. The α and β phases are instable below 437° and 405° respectively. The γ phase is stable only below the solidus.

Zinc-Tin Alloys

The freezing point curve for the zinc-tin series of alloys has been accurately determined by Heycock and Neville.[1] Their measurements were made by means of a platinum resistance pyrometer and all necessary precautions to prevent supercooling, etc., were observed. Their data are given in Table II.

TABLE II

Percent zinc	F. P.	Percent zinc	F. P.
100.00	419.57°	44.88	347.56°
96.85	410.53	38.67	342.70
93.75	402.61	30.77	323.72
83.33	388.38	23.41	297.87
76.92	380.56	16.43	260.80
64.96	370.07	12.58	234.82
58.86	364.37	11.62	228.64
50.93	355.62	10.71	197.79
—	—	00.00	232.00

Aside from the determination of the freezing point curve almost no work has been done on this series of alloys. It is at once evident that only two phases are possible. These might be either the pure components or series of solid solutions. The freezing point curve excludes any compounds.

Microscopically, all the alloys containing 99 percent to 5 percent zinc are inhomogeneous whether chill-cast or annealed. The ingot containing 99 percent zinc shows the characteristic zinc structure with traces of a second phase between the large crystals. This structure was not broken down by annealing at 180° for one and one half months.

All the alloys containing 5 percent and less zinc are homogeneous under the microscope whether chill-cast or annealed. Ingots with more than 5 percent zinc may be inhomogeneous

[1] Jour. Chem. Soc., **61**, 911 (1892); **71**, 383 (1897).

when chill-cast. After annealing at 180°, the 7 percent ingot becomes homogeneous. Alloys having more than 7 percent zinc are not affected by annealing excepting the increase in the crystal size.

The equilibrium diagram is shown in Fig. 4. The solidus is represented by a dotted line between pure tin and seven percent zinc. The exact position of this line has not been located. No definite break was located at 197° in the cooling curve taken on a four percent zinc ingot. The eutectic, therefore, can not extend beyond 95 or 96 percent tin.

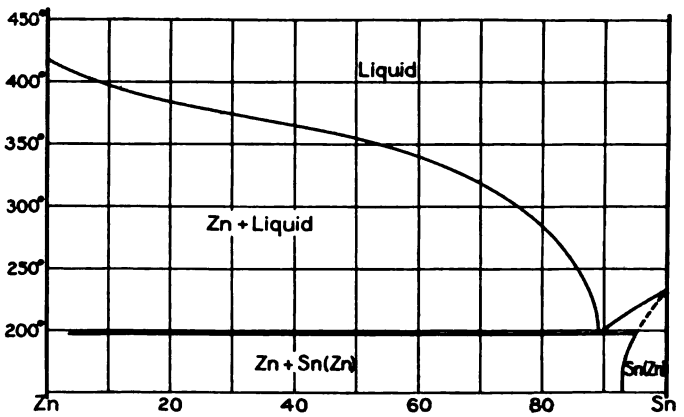

Fig. 4

This series does not contain any hard or brittle alloys. There is a gradation in softness from pure zinc to the pure tin. The pure zinc is harder and more brittle than any of its alloys with tin.

The structure of the zinc-rich alloys is best developed by nitric acid. The structure of the tin-rich alloys is brought out very satisfactorily by electrolytic treatment in a hydrochloric acid solution of stannic chloride.

In conclusion it may be said that the two phases in the zinc-tin equilibrium diagram are pure zinc and a solution of zinc in tin.

The solution of zinc in tin extends over a field about seven percent wide at a temperature of 180°.

Zinc-Cadmium Alloys

The freezing point curve for the zinc-cadmium series of alloys was determined by Heycock and Neville.[1] The curve consists of two branches and, therefore, only two phases can be present in the equilibrium diagram. The freezing point data are given in Table III.

TABLE III

Percent zinc	F. P.	Percent zinc	F. P.
100.0	418.5°	36.3	308.0°
94.9	404.2	32.8	301.0
85.9	381.8	30.0	296.3
71.6	355.0	25.0	285.7
64.7	344.3	21.0	276.1
59.2	336.4	19.2	269.0
54.6	330.7	16.7	264.7
50.6	325.8	10.2	279.4
47.1	321.9	5.8	295.0
43.9	317.1	2.3	309.0
39.8	312.4	0.0	320.5

With the determination of the freezing point curve, the work on the zinc-cadmium alloys stopped.

The freezing point curve for zinc-cadmium is similar to that of the zinc-tin series. The possible phases are also the same in each case.

Microscopically all the alloys between 5 percent and 96 percent zinc are inhomogeneous. This field widens upon annealing and at 217° the 5 percent ingot is homogeneous. The ingot with 6 percent is not homogeneous.

It is difficult to tell whether the chill-cast ingots containing 98 percent zinc or thereabouts are homogeneous. The crystal size is small and the chill-cast field is at most very narrow. Specimens annealed at 217° for about two months become homogeneous at 96 percent zinc content.

The eutectic can be traced to about 96 percent cadmium and 97 percent zinc. Beyond this a definite eutectic heat

[1] Jour. Chem. Soc., 61, 911 (1892); 71, 383 (1897).

absorption is not easily located. On the zinc side of the diagram it is not easy to locate definitely the edge of the field of the series of solid solutions, but long annealing locates it at about 4 percent cadmium.

The equilibrium diagram is shown in Fig. 5.

The solidus on the cadmium side of the diagram is cut by the eutectic isotherm at about 4 percent zinc. On the zinc side the eutectic isotherm cuts the solidus at about 4 percent cadmium. These same solidi are cut by the 217° isotherm at about 4 percent cadmium and 4 percent zinc respectively.

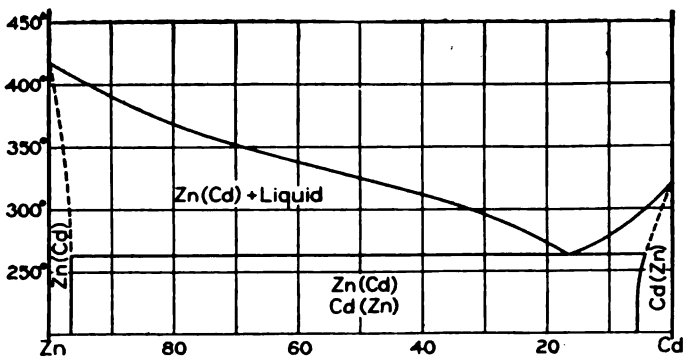

Fig. 5

These alloys may be etched very satisfactorily with nitric acid. Picric acid acts on the cadmium-rich alloys and with a little care gives an excellent surface.

This series contains no hard or brittle alloys. The gradation from the qualities of one metal to those of the other is very uniform. A 50 percent alloy is not very different from either of the components. It is a little harder than pure cadmium, softer than pure zinc, less brittle than zinc and more brittle than cadmium. The two phases in the zinc-cadmium diagram are two series of solid solutions—a solution of zinc in cadmium, and a solution of cadmium in zinc. These extend over a range of 4 and 5 percent respectively at a temperature of 217°. The microscopical and pyro-

metrical evidence agrees with the deductions made from the freezing point curve.

Zinc-Lead and Zinc-Bismuth Alloys

Because of the similarity between these two series of alloys they are here classed together. The freezing point curves have been determined by Heycock and Neville.[1] Their data are given in Tables IV and V.

TABLE IV
Zinc-Lead

Percent zinc	F. P.	Percent zinc	F. P.
100.0	419.2°	84.9	417.6°
99.6	418.7	00.8	318.3
99.4	418.1	00.7	318.3
99.1	417.7	00.3	321.6
99.8	417.3	00.0	327.3
99.1	417.6	—	—

TABLE V
Zinc-Bismuth

Percent zinc	F. P.	Percent zinc	F. P.
100.0	418.8°	26.1	416.6°
99.8	418.4	15.4	416.9 417.8
99.4	417.7	14.2	409.0
97.9	415.9	11.6	287.0
90.4	415.9	7.1	243.0
82.8	415.9	4.1	254.3
73.3	415.9	3.2	254.5
61.6	416.2	1.9	258.0
49.0	416.7	0.0	269.3
36.8	416.9	—	—

From these data it is at once evident that the miscibility of zinc and lead is very slight. Less than 1 percent of zinc mixes with lead at a temperature near the melting point. On the other side of the series the miscibility is only slightly greater.

[1] Jour. Chem. Soc., 61, 911 (1892); 71, 383 (1897).

Castings of varying concentration were made and annealed. The ingots very rich in zinc showed crystals of pure zinc under the microscope. The 99 percent ingot retained its zinc crystalline structure after continued annealing. The ingots rich in lead appeared homogeneous after annealing. An examination of the original castings, however, showed that the lead and zinc had separated and formed in reality two ingots, one very rich in zinc and the other very rich in lead. Analysis of the lead-rich portions showed a varying zinc content of from 0.70–3.00 percent. Analyses of the same ingot could not be made to check closely. This indicated uneven mixing of the two metals which was conclusively shown by microscopical examination. These analyses extended over a series of castings that should have contained from 1–10 percent zinc. These castings were made in vertical moulds, the top portion being rich in zinc.

It is certain from the microscopical evidence that pure zinc separates from zinc-rich melt. The nearness of eutectic concentration to pure lead makes it certain that practically pure lead separates from a lead-rich melt. The fact that the miscibility of the two components is so slight excludes the possibility of making helpful electromotive force measurements.

It is quite sufficient to say that in this series two liquid layers are formed and at the freezing point these consist practically pure zinc and pure lead.

In the zinc-lead series the conditions are very similar to those in the zinc-tin series, the miscibility being a little greater.

Microscopically the zinc-rich ingots are inhomogeneous, even after annealed. Pure zinc crystals separate in the zinc-rich melt. This separation is not different [illegible]

[illegible] 1.5 percent zinc are almost [illegible] and are practically homogeneous [illegible] of alloys containing more than about [illegible] percent zinc show in the microscope a trace of zinc [illegible]

crystals which is more noticeable in 5 percent zinc castings. Fairly uniform castings containing 10 or 12 percent zinc can be made. Castings made for 20–95 percent zinc segregate very badly. The outer portion consists of almost pure zinc while the inner portion of the ingot is very rich in bismuth. If the melt be stirred vigorously before pouring, the ingot will contain globules very rich in zinc or very rich in bismuth. Lead and zinc tend to separate much more quickly and completely than does this series.

Spring and Romanoff[1] have made some determinations on the miscibility of these series; their data are given in Table VI.

TABLE VI

		Zinc-Bismuth				Zinc-Lead			
		Under layer		Upper layer		Under layer		Upper layer	
No.	Temp.	Per-cent Bi	Per-cent Zn	Per-cent Bi	Per-cent Zn	Percent Pb	Percent Zn	Percent Pb	Percent Zn
1	266°	86	14	—	—	—	—	—	—
2	334	—	—	—	—	98.8	—	—	—
3	419	—	—	3	97	—	—	1.5	98.5
4	450	—	—	—	—	92.0	8.0	—	—
5	475	84	16	5	95	91.0	9.0	2.0	98.0
6	514	—	—	—	—	89.0	11.0	3.0	97.0
7	584	80	20	10	90	86.0	14.0	5.0	95.0
8	650	77	23	15	85	83.0	17.0	7.0	93.0
9	740	—	—	—	—	79.0	21.0	10.0	90.0
10	750	70	30	27	73	—	—	—	—
11	800	—	—	—	—	75.0	25.0	14.0	86.0
12	900	—	—	—	—	59.0	41.0	25.5	74.5

These solubilities agree very nicely with those obtained by Heycock and Neville in their freezing point determinations and are probably as near accurate as the experimental error will permit. As yet the miscibility has not been in any case located pyrometrically. Heycock and Neville were unable to find any break in the zinc-bismuth cooling curves above the freezing point.

[1] Zeit. anorg. Chem., 13, 29 (1897).

Fig. 6 shows the equilibrium diagram for the zinc-lead series and Fig. 7 shows the diagram for the zinc-bismuth series. The miscibility curves are represented by means of

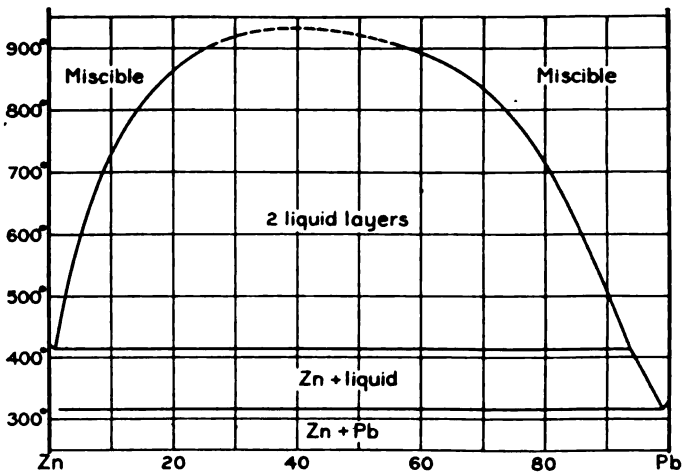

Fig. 6

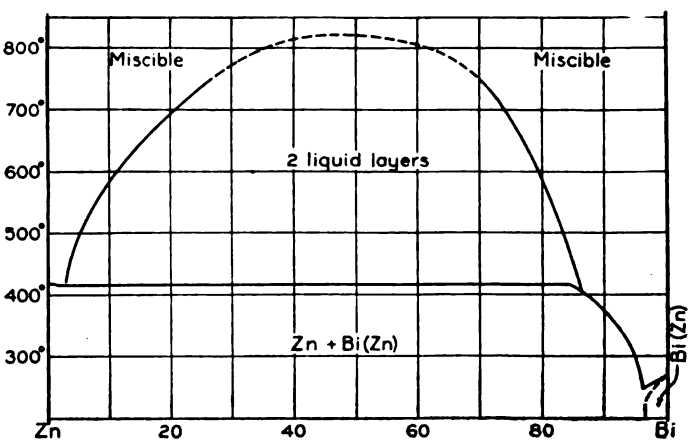

Fig. 7

dotted lines. The consolute temperatures for the two series are very close together, the difference not exceeding 100°.

In conclusion we may say that the zinc-lead series form

two liquid layers, which, according to Spring and Romanoff, become consolute at or near 920°. The two phases separating from the melt are pure zinc and pure lead.

In the zinc-bismuth series two liquid layers are formed which become consolute at near 820°. The phases separating from the melt are pure zinc and a solid solution of zinc in bismuth. The width of this field extends over a range of about 4 percent.

Thanks are here extended to Dr. A. L. Day, of the Geophysical Laboratory at Washington, D C., for the use of apparatus.

This work has been done under the direction of Prof. Bancroft. The expenses have been met by a grant from the Carnegie Institution.

Cornell University

AN EASY METHOD FOR DETERMINING VAPOR-DENSITIES

BY PHILIP BLACKMAN

PART IV[1]

The apparatus here described is an improvement upon that detailed in Part II.

There is no tap, but instead each end of the capillary-tube is furnished with a metal rim with screw-thread on the outside on to which fits a solid metal cap. The bore of the capillary-tube must be of medium diameter (not too wide, nor too narrow).

A "refill" of the following description will be required. A piece of glass tube has one end softened in the blowpipe flame and drawn off to a long, thin, capillary-end. Mercury, or the liquid to be experimented on, can be sucked up into it, and kept there by simply placing the finger over the wide end. Its capillary-end can then be inserted into the bore of the apparatus and by gently loosening the hold over the wide end a thread of mercury, or of the required substance, of any desired length may be injected.

One cap is screwed on to one end of the apparatus. By means of the refill a thread of mercury is inserted in the other end, then a thread of the substance to be experimented on, and finally a second thread of mercury, after which this end is also closed with the screw-cap. The first cap is now screwed off and the required measurements and heating are carried out as already explained.

It is possible (and there is not the slightest need to avoid it) that between the screw-cap and the adjacent mercury-thread may be left a short space of the bore not filled with mercury, but containing air. A little consideration will show that this cannot in any way whatever introduce any error, because the value of L is independent of any changes in this

[1] Continued from the Journal of Physical Chemistry, 13, 537 (1909).

air-space seeing that the other end of the apparatus is open to the atmospheric pressure.

Care will have to be taken not to break off the refill within the bore of the apparatus, as it may be found rather difficult to remove the broken glass.

Note to Parts I-IV

The author now sees quite plainly that the two mercury-threads need not necessarily be perfectly contiguous to the thread of substance between them. This being the case the introduction of the respective threads will be rendered much easier.

Corrigenda

In the Journal of Physical Chemistry, **13** (1909):

Page 426, in the second foot-note, instead of "550" read "745."

Page 428, line 5, instead of "87" read "87, 133."

Page 430, line 25, instead of "H, *n*," read "H, *h*," in the footnote after "(1908)" add "or Journal of Physical Chemistry, **12**, 663 (1908)."

Page 431, line 21, after "(1908)" add "or better, because fuller, Journal of Physical Chemistry, **12**, 668 (1908)."

Page 433, in the footnote, instead of "441" read "4141."

Page 434, line 3, instead of "determined" read "are determined." Line 4, instead of "effected" read "is effected." Line 13, instead of "679, 688" read "679–688."

Page 437, line 15, instead of "the quantity" read "the *positive* quantity."

Addenda

The special apparatus briefly described in the (*Journal of Physical Chemistry*, **12**, 677–678 (1908), **13**, 427 (1909) and *Zeitschrift für physikalische Chemie*, **63**, 639 (1908), **65**, 551 (1909), and very fully detailed in the *Chemical News*, **100**, 13 (1909), is supplied by Messrs. F. E. Becker & Co., Ltd., 17–27 Hatton Wall, London, E. C. (England).

The same makers supply the apparatus described in the

Journal of Physical Chemistry, **12**, 684–686, 690–692 (1908) or *Berichte der deutschen chemischen Gesellschaft*, **41**, 881–883, 4141–4144 (1908)).

The author would be obliged if all those, who feel interested enough to make inquiries concerning the methods and apparatus, would kindly address their communications to "Osborne House, 1, Osborne Str., London, E. (England)" in order to avoid undue delay in the despatch of replies.

Hackney Technical Institute,
London, N. E. (England)

AN ELECTRIONIC THEORY[1]

BY PHILIP BLACKMAN

SEC. 1. The formation of a salt MX from the acid HX and the base M.OH may be represented 'electrolytically' by the equation[2]

$$(\overset{+}{H} + \overset{-}{X}) + (\overset{+}{M} + \overset{-}{OH}) = (\overset{+}{M} + \overset{-}{X}) + H.OH \ldots\ldots (1).$$

The initial and final electrical states differ by the expression

$$\overset{+}{H} + \overset{-}{OH} = H.OH \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2);$$

hence we should expect in the formation of the salt the disappearance of 'electrical conductivity' equivalent to that required by equation (2). This quantity of 'electrical conductivity' will be dependent on (1) the temperature, (2) the molecular concentration (or dilution), and (3) the nature of the acid HX. Suppose these three conditions be fixed, there ought to be a constant quantity for the electrical conductivity corresponding to equation (2).

Let

$$\mu v_{HX},\ \mu v_{M_1.OH},\ \mu v_{M_2.OH},\ \mu v_{M_1X},\ \mu v_{M_2X},$$

represent respectively the molecular conductivities (all measured at the same molecular concentration v, and at the same temperature) of the acid HX, the bases $M_1.OH$ and $M_2.OH$, and the salts M_1X, and M_2X. Then according to the argument just advanced,

$$\mu v_{HX} + \mu v_{M_1.OH} = \mu v_{M_1X} + K \ldots\ldots\ldots\ldots\ldots (3),$$

$$\mu v_{HX} + \mu v_{M_2.OH} = \mu v_{M_2X} + K \ldots\ldots\ldots\ldots\ldots (4),$$

[1] Being a complete summary, revised, and very considerably enlarged tabularly, of a series of papers by the author published in the *Philosophical Magazine*, London Chemical Society's *Proceedings*, *Chemical News*, and *Journal of Physical Chemistry*. The tables on molecular conductivities of salts are quite original, and a great number of the ionic conductivities in the tables are also original.

[2] Compare Phil. Mag. [6], 11, 416 (1906).

where K is a constant. Therefore

$$\begin{aligned}&\mu v_{HX} + \mu v_{M_1.OH} - \mu v_{M_1X}\\ &= \mu v \quad + \mu v_{M_2.OH} - \mu v_{M_2X} \ldots\ldots\ldots\ldots\ldots\ldots (5).\end{aligned}$$

Table I is an illustration of the above; the data (as in all the other tables, unless otherwise mentioned) are taken from the "Physikalisch-Chemische Tabellen", von Landolt und Börnstein; numbers in brackets are from an early edition of that work, the others from the 1905 edition.

SEC. 2. Equation (5) on simplification becomes

$$\mu v_{M_1.OH} - \mu v_{M_2.OH} = \mu v_{M_1X} - \mu v_{M_2X} \ldots\ldots\ldots\ldots (6),$$

which it will be at once evident furnishes a means for calculating the molecular conductivities of salts and bases, whether soluble or insoluble, or stable or unstable, in aqueous solution, whose molecular conductivities cannot be determined by direct measurement.[1] Such results will be found under Table II and Table III. Similarly it can be shown that

$$\begin{aligned}\mu v_{M_1.OH} - \mu v_{M_2.OH} &= \mu v_{M_1X_1} - \mu v_{M_2X_1}\\ &= \mu v_{M_1X_2} - \mu v_{M_2X_2}\\ &= \ldots\ldots - \ldots\ldots\\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7).\end{aligned}$$

Hence,

$$\begin{aligned}\mu v_{M_1X} - \mu v_{M_2X} &= \mu v_{M_1X_1} - \mu v_{M_2X_1}\\ &= \mu v_{M_1X_2} - \mu v_{M_2X_2}\\ &= \mu v_{M_1X_3} - \mu v_{M_2X_3}\\ &= \ldots\ldots\ldots\ldots\ldots\\ &= \text{constant} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8).\end{aligned}$$

Equation (8) it will be seen is identical with the hitherto unexplained fact discovered by Kohlrausch and further extended by Ostwald, see "Lehrbuch der allgemeinen Chemie," II, i, 672.

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[1] Cf. Jour. Phys. Chem., 13, 144 (1909).

TABLE I (TO SEC. 1)

v (at 18°) =	32	10000	2000	1024	1000	500	200	100	50	33·3	20	10	2	1
$\mu v_{\frac{1}{2}H_2SO_4} + \mu v_{KOH} - \mu v_{\frac{1}{2}K_2SO_4}$	(418)	(470)	—	(468)	(422) 468	461	442	(387) 426	409	388	377	(317) 350	(320) 323	(287) 310
$\mu v_{\frac{1}{2}H_2SO_4} + \mu v_{NaOH} - \mu v_{\frac{1}{2}Na_2SO_4}$	(420)	(461)	385	(481)	(413) 459	433	433	(381) 415	395	365	368	(305) 342	(297) 328	(284) 304
$\mu v_{\frac{1}{2}H_2SO_4} + \mu v_{LiOH} - \mu v_{\frac{1}{2}Li_2SO_4}$	(419)	—	—	(482)	—	—	—	(390) 413	—	—	—	(314) 332	(392) 296	(268) 285
$\mu v_{HNO_3} + \mu v_{KOH} - \mu v_{KNO_3}$	(492)	(490)	—	(485)	(439) 485	484	480	(441) 478	474	—	466	(423) 458	432	(374) 413
$\mu v_{HNO_3} + \mu v_{NaOH} - \mu v_{NaNO_3}$	(491)	(480)	—	(494)	(429) 477	477	475	(428) 473	469	—	465	(411) 458	434	(364) 401
$\mu v_{HNO_3} + \mu v_{\frac{1}{2}BaO_2H_2} - \mu v_{\frac{1}{2}Ba(NO_3)_2}$	(473)	—	—	(481)	—	—	—	—	—	—	—	—	—	—
$\mu v_{HCl} + \mu v_{KOH} - \mu v_{KCl}$	(490)	485	—	(489)	(437) 484	473	470	(439) 466	472	—	463	(418) 452	422	(358) 387
$\mu v_{HCl} + \mu v_{NaOH} - \mu v_{NaCl}$	(492)	479	—	(490)	(425) 475	475	473	(433) 471	469	—	463	(408) 454	420	(358) 384
$\mu v_{HCl} + \mu v_{\frac{1}{2}Ba(OH)_2} - \mu v_{\frac{1}{2}BaCl_2}$	(470)	—	—	(490)	—	—	—	—	—	—	—	—	—	—
$\mu v_{HCl} + \mu v_{LiOH} - \mu v_{LiCl}$	(493)	—	—	(491)	—	—	—	(442) 470	—	—	—	444	400	(344) 367
$\mu v_{HI} + \mu v_{KOH} - \mu v_{KI}$	—	—	—	—	—	—	—	—	—	—	—	(426)	—	—
$\mu v_{HI} + \mu v_{NaOH} - \mu v_{NaI}$	—	—	—	—	—	—	—	—	—	—	—	(427)	—	—
$\mu v_{HI} + \mu v_{LiOH} - \mu v_{LiI}$	—	—	—	—	—	—	—	—	—	—	—	(411)	—	—
$\mu v_{HIO_3} + \mu v_{KOH} - \mu v_{KIO_3}$	—	—	—	(482)	—	—	—	—	—	(442)	—	—	—	—
$\mu v_{HIO_3} + \mu v_{NaOH} - \mu v_{NaIO_3}$	—	—	—	(481)	—	—	—	—	—	(441)	—	—	—	—
$\mu v_{CH_3.CO_2H} + \mu v_{KOH} - \mu v_{CH_3.CO_2K}$	—	—	—	—	177	165	154	148	144	140	138	134	127	122
$\mu v_{CH_3.CO_2H} + \mu v_{NaOH} - \mu v_{CH_3.CO_2Na}$	—	—	—	—	171	160	152	147	144	143	141	139	127	117
$\mu v_{\frac{1}{2}H_2C_2O_4} + \mu v_{KOH} - \mu v_{\frac{1}{2}K_2C_2O_4}$	—	—	—	—	292	284	276	273	260	—	250	235	—	170

TABLE II (TO SEC. 2)
Molecular conductivities at 18°

v	$\frac{1}{3}Ca(H_2PO_4)_2$	$\frac{1}{3}Ca_2(HPO_4)_2$	$\frac{1}{2}CaSiO_3$	$\frac{1}{2}Li_2C_2O_4$	$\frac{1}{2}MgSiO_3$	NH_4ClO_3	NH_4IO_3
10000	—	—	—	93	—	119	97
5000	—	—	—	93	—	118	97
2000	—	—	—	92	—	117	96
1000	17	65	152	91	151	116	95
500	17	63	150	90	149	115	94
200	16	61	146	86	145	114	93
100	14	59	141	82	140	111	91
50	—	55	136	78	135	109	90
33·33	11	50	132	—	132	—	89
20	10	53	127	70	127	100	—
10	9	48	120	68	119	96	84
5	—	—	108	59	107	93	79
3·33	—	—	100	—	99	—	73
2	8	36	90	—	88	84	—
1	7	30	73	44	70	—	—

SEC. 3. The foregoing arguments and conclusions may now be most usefully applied to the question[1] of the "relative strengths of acids." Arrhenius showed that if acids be arranged in the order of their relative strengths they were also arranged in the order of their molecular conductivities. The comparison in all cases is so remarkably close that the electrical conductivity method has been accepted as a means for determining the relative strengths of acids. A satisfactory explanation (on the hypothesis of the "degrees of dissociation of acids") has been advanced to establish the connection between the molecular conductivities of acids and their relative strengths, and in this section will be found developed a novel theory as an attempt to supply a proof.

According to Section 1 and Equations (3) and (4) it is evident that had there been in the final solution $\overset{+}{H}$ and $\overset{-}{OH}$

[1] Cf. Chem. News, **93**, 284 (1906), and Proc. Chem. Soc., **21**, 237 (1905).

TABLE III

Molecular conductivities at 25°

$v =$	32	64	128	256	512	1024
$\frac{1}{2}Pb(ClO_3)_2$	94	101	116	120	125	129
$\frac{1}{2}Pb(ClO_4)_2$	103	109	125	129	136	139
$\frac{1}{2}PbBr_2$	108	114	130	134	140	144
$\frac{1}{2}Pb(BrO_3)_2$	85	81	106	109	115	119
$\frac{1}{2}PbI_2$	108	114	128	133	139	143
$\frac{1}{2}Pb(IO_3)_2$	71	77	92	96	101	106
$\frac{1}{2}PbF_2$	84	91	106	109	115	119
$\frac{1}{2}PbMnO_4$	93	98	113	116	122	126
$\frac{1}{2}Pb(NO_2)_2$	119	124	140	144	152	160
$\frac{1}{2}PbSO_4$	96	104	122	128	136	142
$\frac{1}{2}PbCrO_4$	101	109	126	131	138	143
$\frac{1}{2}PbCr_2O_7$	93	97	111	112	117	123
$\frac{1}{2}PbSO_3$	90	98	116	122	129	136
$\frac{1}{2}PbS_2O_8$	98	108	128	132	140	146
$\frac{1}{3}Pb_3(PO_4)_2$	104	115	123	127	130	132
$\frac{1}{2}CuCl_2$	123	125	126	128	130	130
$\frac{1}{2}Cu(ClO_3)_2$	111	114	115	116	118	118
$\frac{1}{2}Cu(ClO_4)_2$	120	123	126	128	128	130
$\frac{1}{2}CuBr_2$	126	128	131	133	133	134
$\frac{1}{2}Cu(BrO_3)_2$	102	104	106	108	109	109
$\frac{1}{2}CuI_2$	125	127	129	130	131	131
$\frac{1}{2}Cu(IO_3)_2$	88	90	92	93	97	98
$\frac{1}{2}CuF_2$	101	103	105	107	108	108
$\frac{1}{2}Cu(NO_2)_2$	134	136	138	139	140	145
$\frac{1}{2}CuSO_4$	110	114	116	118	120	122
$\frac{1}{2}CuCrO_4$	115	119	120	122	123	124
$\frac{1}{2}CuCr_2O_7$	106	107	109	110	111	112
$\frac{1}{2}CuSO_3$	107	110	115	117	120	122
$\frac{1}{2}BaCl_2$	105	113	118	123	128	131
$\frac{1}{2}Ba(ClO_3)_2$	95	101	106	111	115	117
$\frac{1}{2}Ba(ClO_4)_2$	104	109	116	121	125	128
$\frac{1}{2}BaBr_2$	109	114	121	126	130	132
$\frac{1}{2}Ba(BrO_3)_2$	86	94	99	101	105	108
$\frac{1}{2}BaI_2$	109	114	120	127	130	136
$\frac{1}{2}Ba(IO_3)_2$	72	78	83	87	91	94
$\frac{1}{2}BaF_2$	87	92	97	101	102	108
$\frac{1}{2}BaMnO_4$	99	100	104	108	111	114
$\frac{1}{2}Ba(NO_3)_2$	100	106	112	117	120	122
$\frac{1}{2}Ba(NO_2)_2$	120	125	131	137	142	149
$\frac{1}{2}BaSO_4$	98	105	113	120	126	131
$\frac{1}{2}BaCrO_4$	101	110	117	124	129	132
$\frac{1}{2}BaCr_2O_7$	94	99	101	104	107	111

TABLE III—(*Continued*)

$v =$	32	64	128	256	512	1024
$\frac{1}{2}BaSO_3$	91	100	107	112	119	125
$\frac{1}{2}BaS_2O_8$	99	109	118	124	130	135
$\frac{1}{2}SrCl_2$	—	120	125	130	132	135
$\frac{1}{2}Sr(ClO_3)_2$	—	108	113	118	119	121
$\frac{1}{2}Sr(ClO_4)_2$	—	116	123	128	129	132
$\frac{1}{2}SrBr_2$	—	121	128	133	134	136
$\frac{1}{2}Sr(BrO_3)_2$	—	101	106	108	109	112
$\frac{1}{2}SrI_2$	—	121	127	134	134	140
$\frac{1}{2}Sr(IO_3)_2$	—	85	90	94	96	98
$\frac{1}{2}SrF_2$	—	99	104	108	109	112
$\frac{1}{2}BrMnO_4$	—	107	111	115	116	118
$\frac{1}{2}Sr(NO_3)_2$	—	113	119	124	125	126
$\frac{1}{2}Sr(NO_2)_2$	—	132	138	144	147	153
$\frac{1}{2}SrSO_4$	—	112	120	127	131	135
$\frac{1}{2}SrCrO_4$	—	117	124	131	134	136
$\frac{1}{2}SrCr_2O_7$	—	106	108	111	112	115
$\frac{1}{2}SrSO_3$	—	107	114	119	124	129
$\frac{1}{2}SrS_2O_8$	—	116	125	131	135	139
$\frac{1}{2}CaCl_2$	—	117	121	127	131	136
$\frac{1}{2}Ca(ClO_3)_2$	—	105	109	115	118	122
$\frac{1}{2}Ca(ClO_4)_2$	—	113	119	125	128	133
$\frac{1}{2}CaBr_2$	—	118	124	130	133	137
$\frac{1}{2}Ca(BrO_3)_2$	—	98	103	104	108	113
$\frac{1}{2}CaI_2$	—	118	123	131	133	141
$\frac{1}{2}Ca(IO_3)_2$	—	82	86	91	94	99
$\frac{1}{2}CaF_2$	—	96	100	104	105	112
$\frac{1}{2}CaMnO_4$	—	104	107	112	114	119
$\frac{1}{2}Ca(NO_3)_2$	—	109	115	121	123	127
$\frac{1}{2}Ca(NO_2)_2$	—	129	134	141	145	154
$\frac{1}{2}CaSO_4$	—	109	116	124	129	136
$\frac{1}{2}CaCrO_4$	—	114	120	128	132	137
$\frac{1}{2}CaCr_2O_7$	—	103	104	108	110	116
$\frac{1}{2}CaSO_3$	—	104	110	116	122	130
$\frac{1}{2}BaS_2O_8$	—	113	121	128	133	140

ions (*i. e.*, $\overset{+}{H} + \overset{-}{OH}$ = not H.OH but $\overset{+}{H} + \overset{-}{OH}$), the value of K would have been equal to zero; that is, K would represent the molecular conductivity of water at the stated concentration v and temperature.

It has already been shown that K is a constant for each series only, as it varies with the nature of the acid. This can

only be explained on the hypothesis that the variability is due to the fact that the stronger the acid is the greater does the value of the quantity K become, the maximum relative value (at any one concentration and temperature) being reached in the case of the strongest acid. Assuming for the moment that all acids were of equal strength it would be a necessary consequence that

$$\begin{aligned} & \mu v_{HX} + \mu v_{M_1.OH} - \mu v_{M_1X} = K_{(HX)} \\ = & \mu v_{HX_1} + \mu v_{M_1.OH} - \mu v^{M_1X_1} = K_{(HX_1)} \\ = & \mu v_{HX_2} + \mu v_{M_1.OH} - \mu v_{M_1X_2} = K_{(HX_2)} \\ = & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots = \ldots\ldots \\ = & \mu v_{HX_n} + \mu v_{M_1.OH} - \mu v_{M_1X_n} = K_{(HX_n)} \\ = & \text{constant} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9), \end{aligned}$$

(supposing that the terms be so arranged that

$$\mu v_{HX} > \mu v_{HX_1} > \mu v_{HX_2} > \ldots\ldots > \mu v_{HX_n}).$$

In practice, however, this constancy is not observed, as acids are not all of equal strength. The equations may nevertheless be rendered mathematically equal in several ways, the most useful of which, for our purpose, being that which will give quantitative, comparative results. By introducing the factors

$$x_1, x_2, \ldots\ldots\ldots\ldots, \text{ and } y_1, y_2, \ldots\ldots\ldots\ldots,$$

respectively, such that

$$\mu v_{HX} = x_1.\mu v_{HX_1} = x_2.\mu v_{HX_2} = \ldots\ldots\ldots\ldots,$$

and

$$\mu v_{M_1X} = y_1.\mu v_{M_1X_1} = y_2.\mu v_{M_1X_2} = \ldots\ldots\ldots\ldots,$$

the above equations become mathematically equal. Bearing in mind that the greater the equalizing quantities $x_1, x_2 \ldots\ldots$, are, the smaller must be the respective strengths of the acids, it is at once evident that the relative strengths of the acids HX, HX_1, HX_2, etc., are respectively

$$\frac{1}{1}, \frac{1}{x_1}, \frac{1}{x_2}, \ldots\ldots\ldots\ldots\ldots\ldots;$$

or, expressed as percentages,

$$100, \frac{100}{x_1}, \frac{100}{x_2}, \ldots\ldots\ldots\ldots\ldots\ldots$$

But $$x_1 = \frac{\mu v_{HX}}{\mu v_{HX_1}},\ x_2 = \frac{\mu v_{HX}}{\mu v_{HX_2}}, \ldots\ldots\ldots\ldots;$$

therefore, the relative percentage strengths of the acids HX, HX_1, HX_2, etc., are respectively

$$100,\ 100\mu v_{HX_1} / \mu v_{HX},\ 100\mu v_{HX_2} / \mu v_{HX},$$

etc. Table IV, of the relative strengths of some acids at 18°, is especially interesting as it was largely employed in the calculations as explained in the next section.

TABLE IV (TO SEC. 3)
Relative strengths of acids at 18°

v	HCl	HNO_3	$\frac{1}{2}H_2SO_4$	$\frac{1}{2}H_2C_2O_4$ (oxalic acid)	$\frac{1}{3}H_3PO_4$	$\frac{1}{3}C_6H_8O_7$ (citric acid)	$C_2H_4O_2$ (acetic acid)
1000	100	99.4	95.9	48.0	28.1	20.7	10.9
500	100	99.4	93.4	46.0	27.4	19.7	8.0
200	100	99.5	86.5	43.9	24.6	—	5.4
100	100	99.5	80.5	42.7	22.9	11.4	3.9
50	100	99.2	77.9	38.9	20.1	—	2.8
33.33	100	99.2	74.7	39.2	18.4	7.6	—
20	100	99.2	70.3	36.9	—	6.1	1.8
10	100	99.7	64.1	33.3	—	4.5	1.3
5	100	99.4	62.5	32.3	—	—	0.9
3.33	100	99.4	62.5	—	—	—	0.8
2	100	99.0	62.4	23.2	—	0.2	0.6
1	100	100.0	62.6	19.8	7.0	0.18	0.4

SEC. 4. The foregoing results show unmistakably that molecular conductivities are additive properties, the molecular conductivity of any substance in aqueous solution being equal to the sum of the atomic or ionic conductivities of its constituent ions. No such regularity apparently exists between the molecular conductivities of the acids, but if the assumption be made that the ionic conductivity of the $\overset{+}{H}$ ion is a function of the relative strengths of acids, then it is possible to calculate its value, and consequently those of other ions.[1] According to the equations (3) and (4) with the

[1] Cf. Phil. Mag. [6], 12, 150 (1906).

argument thereon, together with the remarks just set forth, the ionic conductivity μv of the $\overset{+}{H}$ ion may be determined from the equations

$$
\begin{aligned}
Rv_{HX} \cdot \mu v_{\dot{H}} + \mu v_{OH'} &= K, \\
Rv_{HX_1} \cdot \mu v_{\dot{H}} + \mu v_{OH'} &= K_1, \\
Rv_{HX_2} \cdot \mu v_{\dot{H}} + \mu v_{OH'} &= K_2, \\
\ldots\ldots\ldots\ldots\ldots\ldots &= \ldots\ldots, \\
Rv_{HX_n} \cdot \mu v_{\dot{H}} + \mu v_{OH'} &= K_n \ldots\ldots\ldots\ldots\ldots (10),
\end{aligned}
$$

(wherein Rv_{HX}, Rv_{HX_1}, Rv_{HX_2}, ... Rv_{HX_n} represent respectively the relative strengths of the acids HX, HX_1, HX_2, ... HX_n, all measured at the same concentration v and at the same temperature. For brevity the sign $\cdot = +$ and $' = -$). The calculations effected by means of these equations (10) are so consistent that the assumptions made above may very reasonably be taken as correct.

As an example the ionic conductivities of the ions $\dot{H}$, OH', $\dot{K}$, and Cl' at 18°, and at concentration $v = 500$ are here worked out fairly fully. R_{HCl}, R_{HNO_3}, $R_{\frac{1}{2}H_2SO_4}$, $R_{\frac{1}{2}H_2C_2O_4}$ and $R_{CH_3CO_2H}$ are respectively 1.0, 0.9946, 0.94, 0.46, and 0.08; and K_{HCl}, K_{HNO_3}, $K_{\frac{1}{2}H_2SO_4}$, $K_{\frac{1}{2}H_2C_2O_4}$, and $K_{C_2H_4O_2}$ are respectively 474, 472, 456, 285, and 163; hence $1.0\,\mu_{\dot{H}} + \mu_{OH'} = 474$, $0.9946\,\mu_{\dot{H}} + \mu_{OH'} = 472$, $0.94\,\mu_{\dot{H}} + \mu_{OH'} = 456$, $0.46\,\mu_{\dot{H}} + \mu_{OH'} = 285$, and $0.08\,\mu_{\dot{H}} + \mu_{OH'} = 163$, from which, by all possible solutions, it is found that the mean values for $\mu_{\dot{H}}$ is 336. Then $\mu_{OH'} = \mu_{H.OH} - \mu_{\dot{H}} \times R_{HCl} = 474 - 337 = 137$; $\mu_{Cl} = \mu_{HCl} - \mu_{\dot{H}} \times R_{HCl} = 376 - (337 \times 1.0) = 39$; $\mu_{\dot{K}} = \mu_{KCl} - \mu_{Cl'} = 126 - 39 = 87 = \mu_{K.OH} - \mu_{OH'} = 233 - 140 = 93$, etc.

In the tables the values given are the means (averages) of values obtained in each case by several calculations.

The letter μ, strictly speaking denoting "molecular conductivity," has been here retained for the sake of avoiding confusion by the introduction of a new distinctive term letter, to represent also "atomic (or ionic) conductivity." The term 'atomic' conductivity is here used in contrast to 'molec-

ular' conductivity, though it may be as well to point out that the term 'atomic' conductivity is rather inappropriate and might be better replaced by the term 'ionic' conductivity. To calculate the molecular conductivity of any salt, acid, or base, repectively, from the ionic conductivities, the equation $\mu v_{M^{\cdot}} + \mu v_{X'}$, $\mu v_{M^{\cdot}} + \mu v_{OH'}$, or $Rv_{HX} \times \mu v_{H^{\cdot}} + \mu v_{X'}$, should be employed.

TABLE V (TO SEC. 4)

Ionic conductivities at 18°

$v =$	1000	500	200	100	50	20	10	2	1
$H^{\cdot}$	337	336	333	330	329	323	313	291	270
$Rb^{\cdot}$	90	89	87	85	85	81	77	—	71
$Cs^{\cdot}$	91	89	87	85	—	—	76	—	—
$K^{\cdot}$	89	89	88	86	83	80	78	67	63
$NH_4^{\cdot}$	85	84	82	80	78	75	72	64	63
$Tl^{\cdot}$	85	85	82	77	76	76	76	—	—
$\frac{1}{2}Ba^{\cdot}$	75	75	69	66	65	57	52	40	36
$\frac{1}{2}Pb^{\cdot}$	76	73	69	63	59	49	41	19	14
$\frac{1}{2}Sr^{\cdot}$	74	70	67	62	61	55	54	36	30
$Ag^{\cdot}$	73	72	70	67	—	62	58	43	40
$\frac{1}{2}Ca^{\cdot}$	69	66	64	60	60	54	44	34	29
$Na^{\cdot}$	66	65	64	61	60	59	58	41	38
$\frac{1}{2}Mg^{\cdot}$	64	60	56	52	47	42	34	32	28
$\frac{1}{2}Zn^{\cdot}$	64	60	56	50	45	40	35	29	19
$\frac{1}{2}Cd^{\cdot}$	—	—	55	46	38	32	26	22	15
$\frac{1}{2}Cu^{\cdot}$	62	55	48	40	33	27	22	—	13
$Li^{\cdot}$	56	54	53	52	51	48	45	40	34
OH'	143	140	140	139	138	135	127	122	109
$\frac{1}{2}CO_3'$	45	41	36	32	27	21	15	12	7
Cl'	40	40	40	40	38	37	37	36	31
NO_3'	40	40	40	40	38	37	36	34	28
Br'	40	39	38	38	38	37	36	36	—
I'	39	38	37	37	37	37	36	36	36
$\frac{1}{2}SO_4'$	37	37	33	32	29	24	22	21	13
SCN'	30	29	28	28	28	28	26	25	24
ClO_3'	28	27	26	26	26	24	21	18	—
F'	21	20	20	20	20	18	16	16	16
$\frac{1}{2}SiO_3'$	12	12	11	19	10	6	—	6	—
$\frac{1}{2}C_2O_4'$	12	12	11	11	9	8	7	6	5
$\frac{1}{3}PO_4'$	11	11	11	9	7	6	5	3	2
$\frac{1}{3}C_6H_5O_7'$ (citrate)	13	12	—	7	—	3	2	1	0.8
IO_3'	8	8	7	7	7	5	2	—	—
$CH_3.CO_2'$	7	6	6	6	5	4	2	1	0.8

TABLE VI (TO SEC. 4)
Ionic conductivities at 25°

$v =$	32	64	128	256	512	1024
$H^{\cdot}$	350	355	360	360	362	363
$Rb^{\cdot}$	88	90	94	96	97	97
$Cs^{\cdot}$	87	90	94	96	97	97
$K^{\cdot}$	85	86	89	93	95	97
$NH_4^{\cdot}$	84	87	90	91	93	95
$Tl^{\cdot}$	80	85	90	93	93	93
$\frac{1}{2}Pb^{\cdot}$	56	64	72	76	84	87
$Ag^{\cdot}$	—	72	74	76	76	76
$\frac{1}{2}Cu^{\cdot}$	61	63	68	71	71	71
$\frac{1}{2}Ba^{\cdot}$	59	65	68	70	74	77
$\frac{1}{2}Sr^{\cdot}$	59	64	67	70	71	72
$Na^{\cdot}$	60	64	67	69	69	69
$\frac{1}{2}Mg^{\cdot}$	58	61	65	69	71	72
$\frac{1}{2}Ca^{\cdot}$	53	63	66	69	70	71
$\frac{1}{2}Ni^{\cdot}$	56	60	64	69	72	74
$\frac{1}{2}Co^{\cdot}$	56	58	58	66	69	71
$Li^{\cdot}$	52	53	56	56	59	62
$\frac{1}{3}Cr^{\cdot}$	27	36	47	58	69	75
$\frac{1}{3}Al^{\cdot}$	11	19	27	36	45	54
OH'	150	153	154	155	155	155
$\frac{1}{3}Cr(CN)_6'$	54	63	67	69	72	75
$\frac{1}{2}S_2O_6'$	52	54	59	66	72	74
$\frac{1}{2}SiFl_6'$	32	48	57	75	—	—
NO_2'	56	57	57	58	60	61
$\frac{1}{3}Fe(CN)_6'$	45	52	58	61	64	66
$\frac{1}{2}Pt(CN)_4'$	51	52	54	56	59	65
Br'	52	53	55	56	57	58
$\frac{1}{4}Fe(CN)_6'$	35	43	50	52	65	66
$\frac{1}{3}AsO_4'$	41	49	55	58	58	58
$\frac{1}{2}S_2O_3$	36	44	49	53	58	60
Cl'	51	52	52	52	53	54
$\frac{1}{2}S_2O_8$	42	49	53	54	55	56
I'	48	49	50	50	51	51
ClO_4'	47	48	49	49	50	51
NO_3'	44	48	48	48	49	50
$\frac{1}{2}SO_4'$	40	42	44	47	50	53
$\frac{1}{2}MoO_4'$	40	42	44	46	49	52
$\frac{1}{2}CrO_4'$	40	41	43	46	48	50
$\frac{1}{2}SeO_4'$	36	39	41	44	47	49
MnO_4'	40	41	42	42	43	44
ClO_3'	38	41	42	42	43	44
$\frac{1}{2}SO_3'$	34	38	41	42	43	44
$\frac{1}{2}WO_4'$	36	38	40	41	44	46

TABLE VI—(*Continued*)

$v =$	32	64	128	256	512	1024
$\frac{1}{3}PO_4'$	—	—	34	39	42	44
$\frac{1}{2}Cr_2O_7'$	34	35	37	37	39	41
$\frac{1}{2}PtCl_6'$	32	36	38	38	39	41
F'	31	32	33	33	34	36
$\frac{1}{4}P_2O_7'$	20	26	33	40	46	49
BrO_3'	29	30	31	32	33	34
HSO_3'	24	27	29	29	31	33
$\frac{1}{2}CO_3'$	14	22	29	37	44	48
AsO_2'	18	18	20	21	24	28
IO_3'	16	17	18	18	20	25
$\frac{1}{2}B_4O_7'$	13	13	13	13	16	19
$\frac{1}{2}B_2O_4$	13	14	14	15	18	20
$\frac{1}{2}S_2O_5$	12	12	12	12	12	12
$\frac{1}{2}SeO_3$	3	10	16	22	31	34

SEC. 5. On comparing the values in Tables V and VI with those given by Kohlrausch in his "Leitvermögen der Elektrolyte" it is found that the conductivities of the $\overset{+}{H}$ and + ions are greater, and the $\overset{-}{OH}$ and — ions are smaller than Kohrausch's values. But on comparing the conductivities of the positive and negative ions among themselves in both the author's and Kohlrausch's tables, the ratios thus obtained are in very close agreement in the respective tables, as is illustrated in Table VII.

In the tables $\mu v_{K^+} = 1.0$, and $\mu v_{Cl'} = 1.0$, respectively, have been chosen for the purpose of calculating the values.

SEC. 6. Another interesting application of the author's theory is that to the subject of the "existence of ammonium hydrate."[1] In the case of ammonium hydrate, $NH_4.OH$, and of ammonium salts, NH_4X, NH_4X_1, etc., the equations (7) and (8) are true for the salts only, the quantity $\mu v_{NH_4.OH} - \mu v_{M_2.OH}$ not being equal to this constant, as is very fully illustrated in Table VIII.[2] It is most peculiar that, whereas

[1] Cf. Chem. News, **95**, 133 (1907).

[2] All quantities indicated by an asterisk (*) were taken from Jour. Phys. Chem., **13**, 145 (1909).

TABLE VII (TO SEC. 5)

"Ionic conductivities" ratios

v (at 180°) =	1000	500	200	100	50	20	10	
$K^{\cdot}$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	From the Author's Tables
$NH_4^{\cdot}$	0.95	0.94	0.93	0.93	0.94	0.93	0.92	
$\frac{1}{2}Ba^{\cdot}$	0.84	0.84	0.78	0.76	0.78	0.71	0.67	
$\frac{1}{2}Sr^{\cdot}$	0.83	0.79	0.75	0.72	0.70	0.69	0.69	
$Ag^{\cdot}$	0.82	0.81	0.79	0.77	—	0.77	0.74	
$\frac{1}{2}Ca^{\cdot}$	0.77	0.74	0.72	0.69	0.72	0.67	0.56	
$Na^{\cdot}$	0.74	0.73	0.73	0.71	0.72	0.73	0.74	
$\frac{1}{2}Mg^{\cdot}$	0.72	0.67	0.64	0.60	0.56	0.52	0.43	
$\frac{1}{2}Zn^{\cdot}$	0.72	0.67	0.64	0.58	0.54	0.50	0.45	
$\frac{1}{2}Cd^{\cdot}$	—	—	0.62	0.53	0.45	0.40	0.33	
$\frac{1}{2}Cu^{\cdot}$	0.70	0.62	0.55	0.46	0.40	0.34	0.28	
$Li^{\cdot}$	0.62	0.60	0.60	0.60	0.61	0.60	0.61	
$\frac{1}{2}CO_3'$	1.1	1.0	0.90	0.80	0.71	0.57	0.40	
Cl'	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
NO_3'	1.0	1.0	1.0	1.0	1.0	1.0	0.97	
I'	0.97	0.95	0.92	0.92	0.97	1.0	0.97	
$\frac{1}{2}SO_4'$	0.92	0.92	0.82	0.80	0.70	0.65	0.61	
$K^{\cdot}$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	From Kohlrausch's Tables
$NH_4^{\cdot}$	0.98	0.99	0.98	0.98	0.98	0.98	0.98	
$\frac{1}{2}Ba^{\cdot}$	0.81	0.81	0.77	0.75	0.70	0.65	0.61	
$\frac{1}{2}Sr^{\cdot}$	0.76	0.74	0.72	0.69	0.65	0.59	0.55	
$Ag^{\cdot}$	0.85	0.85	0.85	0.85	0.82	0.81	0.76	
$\frac{1}{2}Ca^{\cdot}$	0.75	0.73	0.71	0.69	0.63	0.57	0.52	
$Na^{\cdot}$	0.67	0.68	0.66	0.65	0.65	0.64	0.62	
$\frac{1}{2}Mg^{\cdot}$	0.67	0.68	0.64	0.60	0.56	0.50	0.44	
$\frac{1}{2}Zn^{\cdot}$	0.65	0.65	0.61	0.59	0.53	0.48	0.42	
$\frac{1}{2}Cd^{\cdot}$	0.58	0.55	0.48	0.42	0.35	0.27	0.23	
$\frac{1}{2}Cu^{\cdot}$	0.64	0.58	0.50	0.44	0.36	0.29	0.26	
$Li^{\cdot}$	0.53	0.52	0.53	0.52	0.50	0.48	0.46	
$\frac{1}{2}CO_3'$	1.1	1.0	0.95	0.88	0.82	0.73	0.68	
Cl'	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
NO_3'	0.92	0.92	0.92	0.92	0.91	0.90	0.91	
I'	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
$\frac{1}{2}SO_4'$	1.0	0.97	0.92	0.90	0.85	0.78	0.75	

equations (7) and (8) are true for all other bases and salts, ammonium hydrate, as just shown, should form an exception, but an explanation is here advanced to explain this anomaly.

TABLE VIII (TO SEC. 6)

v (at 18°) =	1000	500	200	100	50	20	10	2	1
$\mu v_{KCl} - \mu v_{NH_4Cl}$	0.0	0.1	0.2	0.3	0.3	0.5	1.0	1.0	1.3
$\mu v_{KNO_3} - \mu v_{NH_4NO_3}$	0.9	0.4	0.9	0.2	2.2	0.2	1.4	5.1	8.4
$\mu v_{\frac{1}{2}K_2SO_4} - \mu v_{\frac{1}{2}(NH_4)_2SO_4}$	—	—	—	—	—	—	—	2.9	3.4
$\mu v_{KI} - \mu v_{NH_4I}$	—	—	—	—	—	—	—	0.1	0.5
But $\mu v_{KOH} - \mu v_{NH_4OH}$	206	203	217	219	218	214	210	196	183
$\mu v_{NH_4Cl} - \mu v_{NaCl}$	20.8	20.7	20.4	20.2	20.0	19.5	18.7	19.1	21.2
$\mu v_{NH_4NO_3} - \mu v_{NaNO_3}$	21.7	21.1	19.5	19.8	17.5	18.6	19.4	19.0	21.4
$\mu v_{\frac{1}{2}(NH_4)_2SO_4} - \mu v_{\frac{1}{2}Na_2SO_4}$	—	—	—	—	—	—	—	19.7	19.8
$\mu v_{NH_4I} - \mu v_{NaI}$	—	—	—	—	—	—	—	22.2	24.4
But $\mu v_{NaOH} - \mu v_{NH_4OH}$	177	183	191	194	194	194	192	173	156
$\mu v_{NH_4I} - \mu v_{LiI}$	*32	*32	*31	*31	*30	*30	*30	29.8	32.5
$\mu v_{\frac{1}{2}(NH_4)_2SO_4} - \mu v_{\frac{1}{2}Li_2SO_4}$	*31	*—	—	*29	*28	*27	*26	22.8	25.7
$\mu v_{NH_4Cl} - \mu v_{LiCl}$	*31	*30	*30	*30	*30	*30	*29	30.7	33.6
But $\mu v_{LiOH} - \mu v_{NH_4OH}$	*176	*182	*187	*188	*188	*184	*180	137	125
$^*\mu v_{\frac{1}{2}(NH_4)_2SO_4} - {}^*\mu v_{\frac{1}{2}Li_2SO_4}$	31	—	—	29	28	27	26	27	30
$\mu v_{NH_4NO_3} - \mu v_{LiNO_3}$	31	31	30	31	27	27	28	—	—
$^*\mu v_{\frac{1}{2}(NH_4)_2CO_3} - {}^*\mu v_{\frac{1}{2}Li_2CO_3}$	—	30	32	32	31	30	29	24	22
$^*\mu v_{NH_4Br} - {}^*\mu v_{LiBr}$	31	31	30	31	31	29	27	27	—
$^*\mu v_{NH_4F} - {}^*\mu v_{LiF}$	32	32	31	31	31	31	30	32	27
$\mu v_{NH_4Cl} - \mu v_{TlCl}$	1	1	0	2	—	—	—	—	—
$\mu v_{NH_4NO_3} - \mu v_{TlNO_3}$	12	12	12	12	—	—	—	—	—
$^*\mu v_{NH_4Br} - {}^*\mu v_{TlBr}$	—3	—1	—1	—2	—2	0	0	—3	—
$^*\mu v_{NH_4I} - {}^*\mu v_{TlI}$	—1	—1	—1	—1	—1	—1	1	—3	3

TABLE VIII—(*Continued*)

v (at 18°) =	1000	500	200	100	50	20	10	2	1
$^*\mu_{\frac{1}{2}(NH_4)_2C_2O_4}$ — $^*\mu_{\frac{1}{2}Tl_2C_2O_4}$	—1	—2	—2	—2	—1	—1	1	—	3
$^*\mu_{NH_4C_2H_3O_2}$ — $^*\mu_{TlC_2H_3O_2}$	—2	—1	0	—1	—2	—2	1	—3	2
$^*\mu_{\frac{1}{2}(NH_4)_2SO_4}$ — $^*\mu_{\frac{1}{2}Tl_2SO_4}$	—3	—	—1	—1	—1	—1	1	—4	3
But $^*\mu_{TlOH}$ — μ_{NH_4OH}	228	214	219	220	220	214	212	199	185
μ_{NH_4Cl} — $^*\mu_{AgCl}$	11	11	11	10	11	11	11	9	—
$^*\mu_{NH_4Br}$ — $^*\mu_{AgBr}$	11	11	11	11	12	11	10	10	—
$^*\mu_{NH_4I}$ — $^*\mu_{AgI}$	10	10	11	10	10	10	10	10	11
$^*\mu_{NH_4F}$ — $^*\mu_{AgF}$	12	12	11	11	10	11	10	9	10
$^*\mu_{\frac{1}{2}(NH_4)_2CO_3}$ — $^*\mu_{\frac{1}{2}Ag_2CO_3}$	10	10	11	8	11	11	10	9	10
$^*\mu_{NH_4C_2H_3O_2}$ — $^*\mu_{AgC_2H_3O_2}$	11	11	11	9	11	10	10	11	10
$^*\mu_{\frac{1}{2}(NH_4)_2SO_4}$ — $^*\mu_{\frac{1}{2}Ag_2SO_4}$	11	—	11	11	10	11	10	10	10
$^*\mu_{\frac{1}{2}(NH_4)_2CrO_4}$ — $^*\mu_{\frac{1}{2}Ag_2CrO_4}$	10	10	11	11	11	11	10	—	10
$\mu_{NH_4NO_3}$ — μ_{AgNO_3}	12	11	10	11	—	11	12	—	—
But $^*\mu_{AgOH}$ — μ_{NH_4OH}	196	202	207	208	208	205	200	187	173
μ_{CsCl} — μ_{NH_4Cl}	4	3	3	3	—	—	2	—	—
$^*\mu_{CsBr}$ — $^*\mu_{NH_4Br}$	4	4	4	4	3	3	4	3	—
$^*\mu_{CsI}$ — $^*\mu_{NH_4I}$	3	3	3	3	3	3	3	3	2
$^*\mu_{CsF}$ — $^*\mu_{NH_4F}$	2	2	3	3	3	3	4	5	3
$^*\mu_{CsNO_3}$ — $\mu_{NH_4NO_3}$	2	2	4	3	5	3	1	—	—
$^*\mu_{CsC_2H_3O_2}$ — $^*\mu_{NH_4C_2H_3O_2}$	3	3	3	3	4	4	4	3	3
$^*\frac{1}{2}\mu_{Cs_2SO_4}$ — $^*\mu_{\frac{1}{2}(NH_4)_2SO_4}$	3	—	4	3	3	3	4	4	2
But $^*\mu_{CsOH}$ — μ_{NH_4OH}	210	215	220	221	221	217	212	108	185
$^*\mu_{RbBr}$ — $^*\mu_{NH_4Br}$	4	4	4	2	3	3	4	3	—
$^*\mu_{RbI}$ — $^*\mu_{NH_4I}$	3	3	3	3	3	3	3	3	2

TABLE VIII—(*Continued*)

v (at 18°) =	1000	500	200	100	50	20	10	2	1
$^*\mu v_{RbF} - {}^*\mu v_{NH_4F}$	2	2	3	3	3	2	4	4	3
$^*\mu v_{RbNO_3} - \mu v_{NH_4NO_3}$	2	2	4	3	5	3	2	—	—
$\mu v_{RbCl} - \mu v_{NH_4Cl}$	4	3	3	3	—	3	—	—	—
$^*\mu v_{RbC_2H_3O_2} - {}^*\mu v_{NH_4C_2H_3O_2}$	3	3	3	3	4	4	4	3	3
$^*\mu v_{\frac{1}{2}Rb_2SO_4} - {}^*\mu v_{\frac{1}{2}(NH_4)_2SO_4}$	3	—	4	3	3	3	4	4	2
$^*\mu v_{\frac{1}{2}Rb_2CO_3} - {}^*\mu v_{\frac{1}{2}(NH_4)_2CO_3}$	5	5	3	2	3	3	4	3	2
$^*\mu v_{\frac{1}{2}Rb_2C_2O_4} - {}^*\mu v_{\frac{1}{2}(NH_4)_2C_2O_4}$	4	4	5	3	3	3	3	—	2
$^*\mu v_{RbOH} - \mu v_{NH_4OH}$	210	225	220	221	221	217	212	198	185
$\mu v_{NH_4Cl} - \mu v_{\frac{1}{2}ZnCl_2}$	20	21	23	24	26	28	—	24	—
$^*\mu v_{\frac{1}{2}(NH_4)_2SO_4} - \mu v_{\frac{1}{2}ZnSO_4}$	29	—	32	37	38	41	—	—	45
$^*\mu v_{NH_4Br} - \mu v_{\frac{1}{2}ZnBr_2}$	24	27	21	32	35	35	35	42	—
etc... etc...									
$\mu v_{NH_4Cl} - \mu v_{\frac{1}{2}BaCl_2}$	7	7	—	—	15	17	19	19	—
$\mu v_{NH_4NO_3} - \mu v_{\frac{1}{2}Ba(NO_3)_2}$	12	12	13	15	17	17	13	15	—
$^*\mu v_{NH_4C_2H_3O_2} - \mu v_{\frac{1}{2}Ba(C_2H_3O_2)_2}$	13	13	14	16	17	18	22	23	—
etc... etc...									
$\mu v_{NH_4Cl} - \mu v_{\frac{1}{2}CaCl_2}$	15	16	17	19	20	22	22	—	—
$\mu v_{NH_4NO_3} - \mu v_{\frac{1}{2}Ca(NO_3)_2}$	15	16	17	19	18	22	23	—	—
$^*\mu v_{NH_4C_2H_3O_2} - \mu v_{\frac{1}{2}Ca(C_2H_3O_2)_2}$	18	19	19	16	23	26	23	—	—
etc... etc...									
$\mu v_{NH_4NO_3} - \mu v_{\frac{1}{2}Sr(NO_3)_2}$	16	17	17	23	23	26	27	—	—
$\mu v_{NH_4Cl} - \mu v_{\frac{1}{2}SrCl_2}$	13	14	16	17	19	21	20	—	—
$^*\mu v_{NH_4C_2H_3O_2} - \mu v_{\frac{1}{2}Sr(C_2H_3O_2)_2}$	18	18	20	21	22	24	26	—	—
etc... etc...									

The molecular conductivities of the potassium salts are almost the same as those of the corresponding ammonium salts, and the expression $\mu v_{KX_n} - \mu v_{NH_4X_n}$ is consequently near zero in value as is illustrated in Table VIII. It would be very reasonable to expect that the molecular conductivities of potassium hydrate and ammonium hydrate would also have been almost identical in value (when measured under the same conditions of temperature and concentration).

By means of the equation

$$\mu v_{NH_4.OH} = \mu v_{M_2.OH} + \mu v_{NH_4X_n} - \mu v_{M_2X_n}$$

(a particular form of the general equation (6)), it is possible to calculate the "theoretical" molecular conductivities of ammonium hydrate (see Tables IX and X).

From an examination of the above facts the following is a most reasonable conclusion:

"If the ammonia in aqueous solution were entirely converted into ammonium hydrate, the experimental values for the molecular conductivities would be near the calculated theoretical values. But as the experimental values are far below the theoretical ones, the conclusion is that the ammonia in aqueous solution is only partially converted into ammonium hydroxide. Accordingly, the percentage of ammonia existing as ammonium hydrate in aqueous solution is given by the formula

$$100 \frac{\text{experimental } \mu v_{NH_4.OH}}{\text{theoretical } \mu v_{NH_4.OH}}$$

(see Tables IX and X for the calculated percentages of ammonium hydrate)."

The accompanying Tables IX and X would seem to indicate that the percentage of ammonia in aqueous solution existing as hydrate of ammonia increases with increased dilution, in other words the more concentrated the solution the less favorable are the conditions for the formation and existence of ammonium hydroxide. With the present limited data of molecular conductivities at varying temperatures at one's disposal, it is impossible to determine definitely by the

TABLE IX (TO SEC. 6)

v (at 18°) =	1000	500	200	100	50	20	10	2	1
$\mu v_{KOH} + \mu v_{NH_4Cl} - \mu v_{KCl}$	234.0	232.9	229.8	227.7	224.7	218.5	211.7	196.0	183.7
$\mu v_{KOH} + \mu v_{NH_4NO_3} - \mu v_{KNO_3}$	234.9	234.8	229.1	227.8	222.8	219.2	214.8	202.1	192.4
$\mu v_{NaOH} + \mu v_{NH_4Cl} - \mu v_{NaCl}$	225.8	225.2	224.2	223.6	222.1	219.5	214.1	179.8	162.0
$\mu v_{NaOH} + \mu v_{NH_4NO_3} - \mu v_{NaNO_3}$	226.7	225.6	223.7	223.2	218.5	217.6	214.8	194.5	179.9
$\mu v_{NaOH} + \mu v_{NH_4I} - \mu v_{NaI}$	—	—	—	—	—	—	—	196.3	181.4
$\mu v_{KOH} + \mu v_{NH_4I} - \mu v_{KI}$	—	—	—	—	—	—	—	193.2	175.3
$\mu v_{KOH} + \mu v_{\frac{1}{2}(NH_4)_2SO_4} - \mu v_{\frac{1}{2}K_2SO_4}$	—	—	—	—	—	—	—	187.7	187.0
$\mu v_{NaOH} + \mu v_{\frac{1}{2}(NH_4)_2SO_4} - \mu v_{\frac{1}{2}Na_2SO_4}$	—	—	—	—	—	—	—	188.4	173.8
Average theoretical $\mu v_{NH_4.OH}$	230.1	229.3	226.7	225.6	221.8	218.7	213.8	192.2	179.3
Experimental $\mu v_{NH_4.OH}$	28.0	20.6	13.2	9.6	7.1	4.6	3.3	1.35	0.9
Percentage of $NH_4.OH$ in solution	12.2	9.0	5.8	4.3	3.2	2.1	1.5	0.7	0.5

TABLE X (TO SEC. 6)

v (at 25°) =	512	256	128
$\mu v_{TlOH} + \mu v_{NH_4Cl} - \mu v_{TlCl}$ = theoretical μv_{NH_4OH}	248.9	249.3	246.5
Experimental μv_{NH_4OH}	27.5	19.0	13.4
Percentage of $NH_4.OH$ in solution	11.0	7.62	5.4

preceding method as to what influence rise in temperature may have in increasing or diminishing the percentage amount of ammonium hydrate in solution.

Thus, though ammonium hydrate is theoretically as strong a base (on the electrical conductivity theory) as potassium hydrate, yet, because of the small quantity of ammonia being converted into the hydrate in aqueous solution, it is in practice one of the weakest bases. But this view renders it rather difficult to explain the great solubility of this gas in water.

If 1 gram-molecule of ammonia[1] be dissolved in water to give v liters of the solution, and the proportion of it converted into ammonium hydrate be denoted by q, the concentrations of the combined ammonia, uncombined ammonia, combined water, and uncombined water are respectively

$$\frac{q}{v}, \frac{1-q}{v}, \frac{q}{v}, \text{ and } 1 - \frac{q}{v}.$$

(The letter 'C' denotes 'concentration' and 'Q' a 'constant;' Q_h = hydrolytic constant; Q_e = electrolytic constant.) According to the 'electrolytic dissociation' theory,

$$QC_{NH_4OH} = C_{NH_3} \times C_{H_2O};$$

[1] The author is indebted to Prof. Dr. R. Luther, of Leipzig, Germany, for the following, from "If one grm.-molecule....." to "..... =K Blackman." Subsequently to this communication Prof. Dr. R. Luther pointed out to the author the analogous work of Prof. Dr. F. Walker, Jour. Chem. Soc., 83, 182 (1903). His work, however, is quite independent of Dr. Walker's research.—P. B.

since C_{H_2O} is constant, we have

$$Q_h C_{NH_4.OH} = C_{NH_3} \quad \text{(i)},$$

$$Q_e{}_{NH_4.OH} = C_{NH_4^\cdot} \times C_{OH'} \quad \text{(ii)},$$

$$C_{NH_4^\cdot} = C_{OH'} = \frac{\mu v}{v \mu_\infty} = \frac{a}{v_{\text{Ostwald}}} \quad \text{(iii)},$$

$$C_{NH_4^\cdot} = \text{approximately } \frac{\text{experimental } \mu v}{v_\cdot \text{ theoretical } \mu v}$$

$$= \frac{q}{v_{\text{Blackman}}} \quad \text{(iv)}.$$

$$C_{NH_4.OH} + C_{NH_3} = C_{\text{non-conducting ammonia}}$$

$$= \frac{1 - a}{v_{\text{Ostwald}}} = \text{nearly } \frac{1 - q}{v_{\text{Blackman}}} \quad \text{(v)}.$$

$$C_{NH_4.OH} + C_{NH_3} = C_{\text{non-conducting ammonia}}$$

$$= (1 + Q_h) C_{NH_4.OH} \text{ [from (i)]}$$

$$= \frac{1 - a}{v_{\text{Ostwald}}} = \frac{1 - q}{v_{\text{Blackman}}} \text{ approximately (vi)}.$$

$$C_{NH_4.OH} = \frac{1 - a}{v} \cdot \frac{1}{1 + Q_{h\,\text{Ostwald}}} \quad \text{(vii)}.$$

From (ii), (iii), and (iv) we obtain

$$\frac{Q_e}{1 + Q_h} = \frac{a^2}{(1 - a) v_{\text{Ostwald}}} = Q_{\text{Ostwald}} \quad \text{(viii)},$$

$$= \frac{q^2}{(1 - q) v_{\text{Blackman}}} = Q_{\text{Blackman}} \quad \text{(ix)}.$$

Tables XI and XII illustrate the similarity between these two constants.

According to the "law of mass action" we have

$$C_{\text{uncombined ammonia}} \times C_{\text{uncombined water}}$$
$$= K \times C_{\text{combined ammonia}},$$

(where K denotes a constant) or,

$$\frac{1}{K} = Q = \text{constant}$$

$$= \frac{q}{v}\left(\frac{v}{1 - q}\right)\left(\frac{v}{v - q}\right)$$

$$= \frac{vq}{(1 - q)(v - q)} \quad \text{(x)}.$$

On performing the calculations the values thus obtained for Q are not the same for different concentrations (see lower parts of Tables XI and XII).

TABLE XI (TO SEC. 6)

v (at 18°) =	1000	500	200	100	50	20	10	2	1	Mean
$Q_{Blackman} \times 10^5$	1.69	1.79	1.79	1.93	2.11	2.25	2.23	2.47	2.51	2.09
$Q_{Ostwald} \times 10^5$	1.60	1.86	1.66	1.75	2.34	2.08	1.99	1.69	1.61	1.84
$Q_{(Equation\ x)} \times 10^2$	13.89	9.89	6.15	4.49	2.39	2.14	1.49	0.7	0.5	—

TABLE XII (TO SEC. 6)

v (at 25°) =	512	256	128	Mean
$Q_{Blackman} \times 10^5$	2.66	2.46	2.41	2.51
$Q_{Ostwald} \times 10^5$	2.65	2.44	2.37	2.49
$Q_{(Equation\ x)} \times 10^2$	12.35	8.25	5.72	—

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EXPERIMENTS ON SOLARIZATION

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From a consideration of the literature bearing upon the reversal of the photographic image[1] we find that many conflicting conclusions have been drawn and at times we find the same phenomenon accounted for in two entirely different ways. The differences in many cases are due to slight inaccuracies in the statement of facts. In order to systematize and bring into one general order all the various views as previously held upon the action of solarization, two assumptions have been made as to the behavior of the silver halides[2] and the theory has been outlined in a brief manner as follows:

(1) The action of light on a silver halide corresponds to that of a direct current or of a fairly weak reducing agent. It causes the silver halide to pass through all possible stages.

(2) A fairly strong reducing agent (a developer) does not cause the silver halide to pass through all the possible stages and does reduce certain silver halogen solid solutions or subhalides faster than others which contain less halogen.

In the following, I shall attempt to show how closely the observed facts coincide with the theory and diagrams as previously given. The work has been restricted to two grades of plates, which for convenience of illustrating with the original plates by means of a lantern have been the lantern slide transparency plates of both Seed and Cramer. A standard lantern slide made from a photograph of a prominent French physicist dressed in his academic robes was utilized in much of the work as a copy plate; by the utilization of such a plate with contact printing in front of a Welsbach burner at known distances for specified times much more constancy of the numerous variables entering in the exposures could be obtained than out of doors. By such methods we could feel more certain of changing only one

[1] Bancroft: Jour. Phys. Chem., 13, 1, 181, 269 (1909).

[2] Ibid., 13, 456 (1909).

variable at a time. In out-of-door work, we must consider that the quality of light is never the same for two successive days, and many have obtained erroneous results merely by neglecting to consider this seemingly small factor. When photographs of exteriors were desired, they were obtained by aid of an American Optical Co.'s camera, made about twenty-five years ago, using a number eight stop. As an example of the importance which such a small thing as the deterioration of a Welsbach gas mantle by its continued use had on some of this work, it might be interesting to note that at a given distance for a specified time, entirely different results were obtained when a new or a two weeks old (constantly used) mantle was used. At one time, for the degree of exposure then used, it made the difference between a negative and a positive. Since the actinic value outdoors is much more variable, the importance of accurate observation and check plates is at all times essential in this line of work. In order to continue as nearly as possible in the argument of constancy of variables, one type of developer was used, as it seemed to be best adapted for all grades of work, and the following may be considered as a kind of stock solution.

Solution A	Solution B
1000 grams water 126 grams Na_2SO_3 21 grams hydroquinone	1000 grams water 252 grams Na_2CO_3

Pyro and metol developers were at first tried, but with these, poor results were obtained as compared with those when using the above solutions. This was due partly to the rapidity of such developers. In work on solarization a contrasting plate facilitates the powers of observation to a great degree. All the above work was carried on in an especially prepared dark room which admitted no outside light and was illuminated by means of red light.

As has been noted, it is first necessary to study the qualitative nature of the latent reversed image, and to deter-

mine whether or not we actually are dealing with a silver oxybromide of the general type $AgBr_xO_y$. Following the theory of Abney, that oxidizing agents facilitate the reversal of the image and reducing agents restrain it, the effect of hypobromous acid was determined. The hypobromous acid was first made by the repeated action of bromine water upon mercuric oxide, but the excessive amounts of free bromine present with the acid caused us to adopt a much better method. An aqueous solution of silver nitrate was just saturated with pure bromine water and the straw-colored liquid thus produced was distilled *in vacuo* and the distillate collected under ice water as the hypobromous acid decomposes very readily above 30° C. Such a solution contains approximately 0.74 percent of hypobromous acid; and in all the work the container was surrounded with ice for even at the temperature of the dark room there was present on the surface a little free bromine. Solutions of this acid of varying concentrations were used as a bath for the plate previous to exposure with the following results:

No.	Concentration of the above acid (previous to developing)		Time of exposure behind given plate min.	Distance cm	Result
	Parts of acid	Parts of water			
1	—	—	4	25	positive
2	1	100	3	25	negative
3	1	50	3	25	negative
4	1	10	3	25	negative
5	1	1	3	25	negative
6	5	1	3	25	negative

In all the above experiments there was no action that would tend to show the production of a positive image while in No. 2 there was but a slight difference between the appearance of this and a plate without previous immersion developed under the same conditions. As the concentration of the hypobromous acid was increased, there was a decided

elimination of fog and for No. 4 an ideal negative was produced of remarkable clearness. The presence of the hypobromous acid then may be considered not to facilitate reversal. Its effect is to produce clearness or in other words for the amateur we have an ideal solution for the production of a transparency were it not for the ease of its decomposition, and hence the disagreeable manner of manipulation. If oxidizing agents did facilitate the reversal of the image we should expect that it would be caused, in the case of a long exposure, by the reaction of the moisture in the film with the bromine liberated forming hypobromous acid which in turn would act as a vigorous oxidizing agent on the normal image. From the above data it appears that this is not the case.

The action of oxidizing agents was studied additionally by determining the effect of permanganate solutions, because Abney[1] seemed to think that reversals took place much more rapidly with potassium permanganate, potassium dichromate, etc. A solution of 0.1 gram of potassium permanganate in 200 grams of water was made and the following results were obtained by an immersion in this bath with subsequent exposure and development.

No.	Concentration		Time of exposure min.	Distance cm	Result
	g. $KMnO_4$	g. H_2O			
1	0.0	—	4	25	positive
2	0.1	200	3	25	clear negative
3	0.1	200	3	25	clear negative
4	0.1	200	3½	25	clear negative
5	0.0	—	3½	25	fogged negative
6	0.1	200	4	25	clear negative
7	0.1	200	5	25	transparent positive

After exposure, the plates were developed in one part of solution A, one part of solution B of the stock developer, with an equal volume of water. In many of the films there were irregular stains due to the drying of the permanganate

[1] Phil. Mag. [5], 10, 204 (1880).

in spots, so that an ideal image was not obtained in all cases. The effect could be easily detected however and in all cases there was an appreciable and distinct clearing effect over the corresponding unimmersed plate. This is shown by the difference between Nos. 4 and 5. As all the above plates were from the same original emulsion and as each variable was kept very closely under control, there is no evidence of an oxidizing agent producing solarization. In fact the difference between Nos. 1 and 6 for the same degree of exposure seems rather startling at first; but when we consider that there is a certain amount of absorption of light by the wet permanganate it will account for the seemingly checked reversal, and is therefore not an important point. More work was carried out with another concentration of permanganate with the same results as previously obtained.

No.	Concentration		Time of exposure min.	Distance cm	Result
	g. $KMnO_4$	g. H_2O			
1	0.0	—	4	25	positive
2	0.1	100	3	25	negative
3	0.1	100	3½	25	clear negative
4	0.1	100	4	25	negative
5	0.0	—	3½	25	fogged negative
6	0.1	100	4½	25	fine positive

With this concentration more trouble with stain was encountered than in the previous case, but it was always noticeable that the oxidizing agent had a tendency to improve the tone of the plate rather than to produce solarization. Even when a positive was obtained by increased exposure as in No. 7 of the first case or No. 6 of the last, a much better positive was obtained than in the absence of permanganate. This is just the point to the whole experiment for what Abney really meant was that for an equivalent exposure with immersion a much better positive is obtained than without such a treatment. We obtained lantern slides of Nos. 1 and 7 and Nos. 1 and 6 which showed this effect

remarkably well. The explanation for this action has been previously given in presenting the theory, but it is perfectly evident that, in the absence of an oxidizing agent, a sufficiently long exposure produces an intense reversed image and a feeble normal image on the plate after development. The presence of an oxidizing agent retards the formation of the last image, and we have the production of a better positive because our final product is the difference that we see between the two images on the same plate. From these data, taken with closely checked plates under practically constant conditions, we find that the oxybromide theory is of no avail and must conclude that the latent normal image consists at least in the beginning of silver and bromine only.

The various stages which a plate undergoes in the study of solarization are well known, but if different exposures are developed for a given time under the same conditions the following hypothetical curve will show very clearly the effect of light.

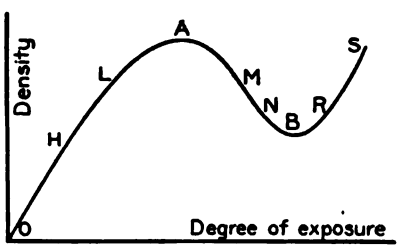

Fig. 1

Although this is by no means a quantitative curve, still it is verified by the following qualitative data:

No.	Length of exposure	Distance from Welsbach cm	Type
1	10 sec	25	negative (O—H)
2	3½ min	25	partial (L—M)
3	4½ min	25	positive (M—N)
4	30 min	25	negative (R—S)

From this we see that there are three distinct stages and that the final one is a negative which is undoubtedly due to the reduction of silver bromide to metallic silver by light. It was interesting to watch the continuous action. In No. 1 we have the degree of exposure of the high lights as point H greater than those of the shadows and the resulting picture is a negative. For No. 2 we have the degree of exposure of the high lights at a point similar to M with the shadows back on L and we get a partial negative, with the high lights reversed and the shadows as negatives. As we continue from M to N we have our high lights as the lightest and a positive results. With a very long exposure we obtain a negative of reduced silver. The above diagram then enables one to picture clearly the progress of the three distinct stages, and although the above was obtained with exposures behind the standard lantern slide with the stock developer, still with increased exposure the same results may be obtained using a camera and photographing landscapes.

It is a well-known fact that by using a weak developer the best results may be obtained with over-exposed plates, or the other method is to restrain the developer by means of bromide, etc. To account for this it has been pointed out[1] that the rate of development of an unexposed plate is nearly zero, that there are definite rates of development for exposed plates, and that the developability of the final silver is zero. We must consequently have at least one maximum rate of development for a specific developer as the composition of the halide changes under composed silver bromide to silver. The action of a developer of two different concentrations was studied in the light of the diagram as previously shown. The ordinates are rates of development, while the degree of exposure was plotted as abscissas. It was also considered that we might use the variation of undecomposed silver bromide to silver as abscissas since beyond a certain point the degree of reduction of the silver bromide is some direct

[1] Bancroft: Jour. Phys. Chem., 13, 457 (1909).

function of the intensity of the light by the time of exposure. In the following experiments the stock developer was used and its applications to Fig. 2 will be easily seen.

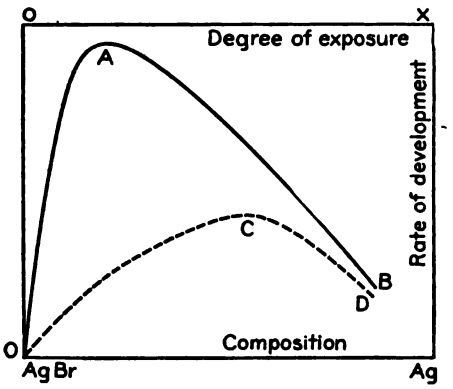

Fig. 2

No.	Time of exposure min.	Distance from Welsbach cm	Developer parts			Type
			A	B	H_2O	
1	4	25	1	1	2	positive
2	4	25	1	1	5	poor positive
3	4	25	1	1	10	mongrel
4	4	25	1	1	20	negative
5	6	25	1	1	20	fog
6	7	25	1	1	20	positive

From this it was seen that for a normal developer we have a higher rate of development than for a dilute one, and hence we are able to get a fair negative with a developer represented by OCD for the same exposure which would produce a poor image with the developer as represented by OAB. From the above we see that for two exposures of the same time Nos. 1 and 4 we can obtain a positive by normal development but a negative by weak development. The reversal of an image is therefore checked by the use of a weak or restrained developer. For exposures below 3 1/2 minutes in the above work we are along the curve OA and for all grades of de-

velopers obtain negatives but of varying degree of contrast according as the degree of dilution is decreased. For the normal developer an exposure beyond A produces a positive as No. 1 shows. It requires nearly twice the length of time to produce a positive in the weak developer, as is indicated by No. 6. In the above work all of the plates were developed for the same length of time in order to obtain comparable results. The important point is to notice that we have confirmed the fact that point C lies to the right of A as seen from number one and four, but as to the relative positions of the curves beyond C we have not even qualitative data as this is unimportant at present.

By first defining a depolarizer as any substance which eliminates bromine in this particular work, we may prevent the confusion arising from the term reducing agent. After we had observed the manner in which oxidizing agents behaved under carefully checked conditions, it seemed that the next logical step was to determine the real and not apparent effect of the depolarizer especially in the light of the previous theory and diagrams.

Abney found that on bathing a plate before exposure in a 5 percent solution of sodium nitrite for a long time, the reversal was prevented even for long exposures. Such a fact was cited in favor of the oxybromide theory. Likewise Lüppo-Cramer confirmed Abney's results by dipping dry plates for about two minutes in a 2 percent solution of sodium nitrite and then drying before making the exposure. Subsequent development after an exposure along with check plates which solarized presented only dense negatives. Lüppo-Cramer also noted that such a plate as the above changed more in a few minutes exposure to diffused daylight than the unwashed check plates after several hours' exposure to direct sunlight. In this work apparently a 2 percent solution of sodium nitrite was employed; however, after drying, the real concentration was not known. From such a result Abney believed the cause of the forcing back of solarization was the reducing action of the nitrite, while Lüppo-Cramer main-

tains, from the analogous action of sulphites, etc., that there is an acceleration in the splitting off of bromine from the silver bromide and that really we do not know why these act in such a manner. However, Eder found that even the traces of silver nitrate which cling to the silver bromide after long washing with water cause a very dense plate, masking the reversal, but a short treatment with nitric acid (sp. gr. 1.20) after the exposure caused a positive to appear. Reversal has taken place in reality, but has been masked which is quite an important point.

With a knowledge of such actions and the previous theory, solutions of sodium nitrite were made up and the plates given a preliminary bath in those solutions. Development in the regular stock developer brought out the following:

No.	Conc. $NaNO_2$	Parts of H_2O	Time of immersion	Exposure	Type
1	1	50	2 min.	30 sec.	dense neg.
2	1	75	2 min.	1 min.	dense neg.
3	1	100	2 min.	1 min.	dense neg.
4	1	150	2 min.	1 min.	dense neg.
5	1	200	2 min.	50 sec.	blurred neg.
6	1	300	2 min.	50 sec.	positive
7	1	100	rapid with slight washing in water	5 min.	fogged pos.
8	0	wet plate	none	1½ min.	positive
9	1	300	2 min.	1½ min.	partial

We see from this that it is possible to obtain positives even in the presence of nitrites with the type of plates and the source of light as used and with development in the regular stock solution. Previous failure, then, was due to the presence of too high a concentration of nitrite in the film, to too long an immersion, or, as was undoubtedly more often the case, to too long an exposure for the given concentration of nitrite. Under such conditions only the third stage as previously given was obtained, and the rapid reduction to metallic silver

in the presence of nitrite by too long an exposure always produces this third stage of the second negative.

After such observations, a continued study was made on the action of depolarizers in the form of a hydroquinone developer present in the film during exposure. The solution, for the sake of uniformity, was some of the regular stock developer. With very rapid work and after many unsuccessful trials the following data were obtained which could be easily checked after proper experience in the manipulation and haste required for such work.

No.	Concentration of developer			Length of exposure min.	Distance from Welsbach cm	Type
	Sol. A	Sol. B	H_2O			
1	1	1	10	1	125	negative
2	1	1	10	1½	125	partial
3	1	1	10	2	125	partial
4	1	1	10	3	125	positive
5	1	1	10	3½	125	partial
6	1	1	10	4	125	negative
7	1	1	10	5	125	negative

In order to avoid the intense fog 10 cc of a 10 percent solution of potassium bromide was added to 50 cc of the above developer. The final development was accomplished by means of the following stock developer:

Solution A, 20 cc; Solution B, 40 cc; 20 percent KBr, 2 cc.

With these plates there was a great tendency for blotches and irregular development, but this was eliminated to a slight extent by shaking the plate vigorously before exposure and by taking care to obtain a surface of contact with the copy plate as free from air bubbles as possible. In all cases the plates were far from perfect, yet the principle could be shown very clearly, and here again we find the depolarizer acting as a masking agent rather than a restrainer of solarization. The general result obtained by one unfamiliar with the work would be a negative due to over-

exposure and the excess of silver thus deposited. It was interesting to note that with No. 3 where the change occurs from the first stage to the second, or from a negative to a positive, the high lights were even in this case the first to be transparent and fall in line with the requirements of Fig. 1. However, when the transformation from the second to the third stages, or from positive to final negative occurs, the high lights were the first to reverse again, and No. 4 was utilized as a slide showing the shadows as still positive while the high lights were a dense negative. Since the time for a solarization is so greatly decreased this last mongrel effect might be in some cases produced, and taken as the next stage towards solarization. By noticing the high lights we have an indication as to what portion of the course we are on, and the time of exposure may be controlled accordingly. In a way the above coincides with the general belief as stated by Trivelli[1] that the stronger the developer and the longer one develops, the more marked is the solarization. By regulating the development one can prevent or cause the appearance of solarization[2] and we have increased the rate of the reaction when we have a depolarizer present.

Positives from Short Exposures

According to our previous statements the presence of a developer or depolarizer in the film during exposure to light should make the image appear as a negative or positive, depending upon the concentration of the developer and the degree of exposure. It should therefore be possible by carefully controlling the concentration of the developer within the film to obtain a positive upon very rapid exposures. In this case as with the previous ones, the same copy lantern slide was used with a Welsbach burner as the source of light, but for considerable time only bad negatives or fogged plates were obtained after a short exposure. It also required extreme haste between the time of exposure and the time of

[1] Bancroft: Jour. Phys. Chem., 13, 297 (1909).
[2] Eder's Handbuch der Photographie, 3, I, 114 (1902).

final development; however, after using every possible precaution and by freeing the contact surfaces from air blotches the following results were obtained although the plates were somewhat spotted.

No.	Time of exposure sec's.	Developer in film			Type
		Sol. A	Sol. B	H_2O	
1	1–2	5	5	100	negative
2	1–2	5	10	100	negative
3	1–2	10	10	100	negative
4	1–2	15	10	100	partial
5	1–2	15	15	100	positive
6	1–2	20	20	100	negative
7	1–2	25	25	100	negative

The plates were immersed in the solution of the given developer for two minutes and then the surface was made more uniform by sweeping the plate through the air for a few seconds. The final development was accomplished by means of the same developer as used in the previous cases. By varying the composition of the developer and the degree of exposure it was found possible to obtain nearly any degree of thickness in the film. However, this method has but narrow and limited application inasmuch as it requires too hasty a development after the exposure and too long a practice to obtain just the right conditions for any specified developer. The slightest over-development causes disastrous results. It was interesting, however, to see how much acquaintance with a process has to do with its successful operation, as well as the importance of changing only one variable at a time.

With the above data some interior work was attempted in order to see to what extent an exposure could be decreased for a negative and hence apply the theory practically. For the illumination of a room on a cloudy day at about four o'clock in the afternoon of the month of May it was found that with the correct concentration of a developer in a film

the time for exposure could be decreased appreciably as the following plates indicated. The results depended upon the personal observation rather than upon density measurements.

No.	Time of exposure sec.	Developer in film			Type
		Sol. A	Sol. B	H_2O	
1	1	1	1	0	good negative
2	12		none		good negative
3	1		none		thin negative
4	1	1	1	5	thin negative
5	1	2	2	0	clouded plate

The above was taken with the camera mentioned previously. Although the illumination was rather poor, still there was present an appreciable amount of the blue rays. This might be of some value in certain cases where interiors were of such a nature as would demand a short exposure in the presence of weak illumination. This method also requires the proximity of a dark room in which to accomplish development immediately so it has decided limitations. For final development the same stock solution was used as before. The annoying feature of such a process appeared when its application in place of flashlight powders was undertaken, for with the artificial illumination by electric light only badly fogged plates could be obtained when a depolarizer was present in the film during exposure. At first this was accounted for by postulating: that the quality of the light was entirely different than in the previous experiment, so that there was a noted absence of the blue and active rays of light; or that the action of the light was so slow as to allow the developer to reduce as rapidly as the light sensation acted and hence cause a uniform fog. We must confess that there are as yet important factors, such as the quality of the light, etc., entering into this work. Until such effects have been studied, the data as given above cannot be considered ab-

solute. More must also be known about the decomposition of the silver bromide by the first traces of light before the visible image is developed in order to solve this method of sensitizing. However, from these preliminary observations for certain qualities of lights it would seem that we have again the confirmation of the previously stated theory.

After clearing up a few of the elementary snags in this line of work and having a little knowledge as to the real action, it was attempted to learn how to produce positives with very rapid exposures in the most practical way. Nipher[1] has shown under what widely different conditions a positive may be obtained by an exposure to white light after the exposure to the specified object. However, a fairly long exposure was required in order to obtain good positives. The same general idea was followed in our attempt to produce rapid positives, and as white light failed to give good results the action of various colored lights was first studied. Solutions of varying concentrations of copper sulphate, potassium dichromate, cyanine, fuchsine and orange crystals (a dye) were made up and, with the proper dilutions of these various materials, light absorption bands covering any portion of the spectrum could be obtained. Potassium dichromate at a proper dilution served as a fine filter for the blue bands, while orange crystals make a fine filter for all but the green-blue portion. In this work the cell serving in the capacity of a filter was placed in front of the Welsbach burner which was used in the previous experiments. By properly enclosing the excess light the light values along the whole system could be controlled. Before utilizing these filters the light was examined by means of a spectroscope in order to tell exactly what lights were being used. Instantaneous exposures were then taken and by developing with the regular stock developer in the presence of the following lights we obtained:

[1] Trans. Acad. Sci., St. Louis, **10**, 210 (1900).

No.	Light composition	Distance of developing solution cm	Type
1	red	25	fine negative
2	yellow	25	fine negative
3	green	25	fine negative
4	blue	25	fogged thin pos.
5	blue-violet	25	fogged plate
6	yellow-green	25	good negative
7	green-blue	25	positive

It was surprising to see the splendid quality of the negative developed even in the green rays. When the blue-violet is used a very rapid action takes place with the result of a thick fog; however, with the continuation of the green-blue at last positives were obtained. Even for exposure during development to white light the results were far inferior to the green-blue combination. In spite of the fact that we had anticipated a greater sensitizing effect for this mixture, only comparatively thin positives resulted from rapid exposures. Although this work failed to bring us any nearer the solution of instantaneous positives, it did, however, give an insight into what were the active rays of light during such an operation, and this may aid in some way in later studies.

When we examine Fig. 2 it may be seen that if the reducing power of the developer is increased, the maximum of the curve changes. Consequently by increasing the alkalinity of the developer we should change our conditions to a more suitable method of development. When the plates were given a rapid exposure and developed in the green-blue light combination with the following stock developers we obtained decidedly different results as may be seen.

With No. 3 the plate resembled a very thin transparency positive. With No. 5 a splendid dense image was obtained. The least over-development in the light caused a surface fog; but, with proper precautions, plates from instantaneous

exposures were obtained which were too dense to make satisfactory lantern slides. Although the general method of procedure as adopted in the last two experiments for the production of rapid positives is well known, still we have shown that since the sensitiveness of the plate changes during exposure for lights of given wave lengths we can control the amount of contrast by varying the wave lengths of the fogging lights and can hence obtain more dense plates for shorter exposures.

No.	Developer used			Type
	Sol. A cc	Sol. B cc	20 percent KBr cc	
1	20	10	10	thin fogged positive
2	20	20	10	thin positive
3	20	30	10	thin positive
4	20	40	10	more intense positive
5	20	50	10	quite dense positive
6	20	60	10	badly fogged

Another general method of rapid positive production involved a slow change in the latent image before final development. There are many cases on record where films have remained in a camera for several months or perhaps years and upon development have resulted in partial or total positives. This has been accounted for by the fact that the silver bromide has been reduced to some lower stage by slow decomposition and in that way resembles the effect produced by an over-exposure. If such is the case we can utilize this as a method for obtaining more dense positives on a short exposure, but under conditions which may be more easily controlled. The plates were given a rapid exposure as before and left in varying dilutions of the stock developer for varying times, and then were finally developed by aid of the green-blue fogging light with the results in table below.

The desired contrast in the densities of Nos. 5 and 6 when compared with No. 1 would indicate that here we had a slow decomposition aiding very much in the final quality

of the positive obtained. The final development in these cases required decidedly less time for the correct density than in the case where no slow action was allowed to take place. In the previous experiments the fogging time while in the developer was very close to two minutes. With the slow decomposition the best results were obtained with a fogging period of slightly less than one minute.

No.	Initial developer			Time min.	Final developer			Type
	Sol. A cc	Sol. B cc	H_2O cc		Sol. A cc	Sol. B cc	20 % KBr cc	
1	0	0	0	0	20	30	10	thin positive
2	1	1	200	30	20	30	10	thin positive
3	1	1	100	30	20	30	10	thicker positive
4	1	1	75	30	20	30	10	more dense
5	1	1	75	50	20	30	10	good positive
6	1	1	50	30	20	30	10	good positive
7	1	1	50	10	20	30	10	thin positive

Before continuing with the remainder of the sensitizing experiments it might be well to review briefly the three previous general methods for the production of positives from rapid exposures. In the first, where we exposed with a dilute developer in the film, the light acts in the presence of a strong depolarizer with the consequence that for a given exposure the chemical action is greatly increased. This method was extremely poor and such a wet-plate process would never receive any general application. The second was a dry method and, since the fogging green-blue wave-length of light can be readily prepared, this would seem to be quite practical provided direct positives of good density were desired (as will undoubtedly never be the case). The third method involving a slow reduction requires too long a time with no better results than by exercise of proper care in the second method, hence its application may be somewhat limited. However, the theoretical side of the whole presents very interesting aspects in which all three of the above methods have their decided bearing as has been shown.

Carey Lea[1] has suggested the analogy of the action of sodium hypophosphite to that of light, showing that we obtain a negative effect with a 25–30 percent solution, while with a 2 percent solution we have the positive action with silver bromide plates. If this solution had an action similar to that of light we were obtaining decided contradictions to our previous results, since with a concentrated solution or an intense light we obtain a negative while with a dilute solution or a weak light we obtain a positive effect. Upon the supposition that the final negative effect was that of the third stage of our original diagram there should exist another negative for dilutions below that of 2 percent. With the idea of determining this concentration we began our study with the faint hope of its application to rapid positives. Several plates were immersed after exposure in sodium hypophosphite solutions of varying concentrations, but in no case was there any appearance of reversal. As the concentration increased, the thickness of the film was found to decrease. This seemed to indicate that we were dealing at least with a solvent action, so unexposed plates were treated in the following manner and these results were obtained upon development in the regular stock developer without washing.

No.	Conc. of sodium hypophosphite Percent	Time of immersion	Type
1	1	1 min.	No darkening; positive
2	2	"	" "
3	3	"	" "
4	10	"	" "
5	15	"	" "
6	20	"	" "
7	25	"	" "
8	30	"	Film is mostly dissolved
9	35	"	Film dissolved
10	40	"	" "
11	35	2 sec.	Blackening; negative
12	40	"	" "

[1] Am. Jour. Sci. (3), 33, 482 (1887).

From this we find that sodium hypophosphite may act as a reducing agent or as a solvent for silver bromide according to whether the plate remains in the solution for a long or a short time. Immersion for a long time with a concentrated solution produces a positive effect since the solvent action is greater than the reducing. With a short immersion we have the reducing action as the important feature and we obtain a blackening of the silver bromide. In all the above work only half of the plate was immersed in the solutions in order to make the correct comparisons with the untouched bromide. We see then, that Lea's apparent reversals with dilute, and non-reversals with concentrated sodium hypophosphite are due to the action of this reagent both as a solvent and a reducing agent towards silver bromide, and hence its action is really not analogous to that of light.

Another method for the production of positives with extremely rapid exposures was that of Waterhouse, using a thiocarbamide solution. Since but few logical explanations had been given for the action of this developer a more detailed study was pursued with the aim of possibly finding the application of other substances in a similar manner. Lüppo-Cramer[1] decided from his work on this Waterhouse developer that metallic silver is precipitated from the solution, obtained by the action of the thiocarbamide dissolving some of the silver bromide, and hence a heavier deposit on the portions where we have the large amount of silver bromide with the result of a reversal. However from our results obtained with other materials it was suggested that the real action of the thiocarbamide might be due to a change in the curve of the second diagram[2] similar to the case of displacement in the experiments with the weak and strong developers. The first point to be tested was the fact that on a very short exposure a positive was obtained and not a negative as would follow from the previous diagram. The following experiments were tried in an attempt to locate the first negative.

[1] Photographische Probleme, 189 (1907).

[2] Bancroft: Jour. Phys. Chem., 13, 459 (1909).

No.	Developer				Time of exposure	Type
	Sol. A cc	Sol. B cc	H_2O cc	Thio-urea sol. cc		
1	25	25	5	20	2 seconds	fogged plate
2	25	25	5	20	1 second	partial positive
3	25	25	5	20	Instantaneous	positive
4	25	25	5	20	Fraction of sec. (poor illum.)	fogged plate

The above pictures were taken by means of a camera in a lecture room where the illumination could be changed by means of dark shades. Below a certain exposure for the given illumination only a fogged plate could be produced without the least trace of a developable image. The lowest good result obtained was then a positive and since we could not obtain a negative with shorter exposure the previous hypothesis fails to account for the production of a positive with such a short exposure.

The thiocarbamide used in the above experiments and also in all the following was made by heating ammonium sulphocyanate for quite a time until the dense white fumes were given off in abundance; the material was then cooled rapidly to 80° C and dissolved in an equal volume of water. Upon standing, fine needle-like crystals of thiocarbamide were obtained. A standard solution of 1 gram of these crystals in a liter of water was made and it was this solution that is mentioned in the above data.

Several plates corresponding to No. 3 in the above were made in order to examine what really happened in each case. On every plate a negative first appeared followed by a positive. The appearance of both images could be detected after fixing with hypo, because, by reflected light, the negative image appeared on the surface side, while the positive image readily appeared upon the glass side of the film. On all of the plates there seemed to be a fairly dense surface deposit and the idea of a screening effect was brought forward, but

an exposure with the plate's glass surface out for the same conditions as No. 3 in the above still yielded a positive, and no negative was observed to appear upon the film surface side during development as was true in the other cases. From these results we must conclude that the effect is not due to a screening action. In order to determine whether the negative appearing during such a development was a normal negative or not, the plate was given a preliminary development in a weak solution. Final development in the thiocarbamide developer produced the same results as in the first case and since the negative was obtained thus we must conclude that it is the normal negative with which we are dealing. Whether the negative image was essential to reversal or not was shown by developing first in the weak developer of the following composition: Sol. A, 5 cc; Sol. B, 5 cc; H_2O, 25 cc; and after dissolving out the negative image thus produced by means of permanganate solution a positive was developed with the regular thiocarbamide solution. Instead of utilizing permanganate as a solvent for the silver, far better results were obtained with chromic acid since a more compact film is left than is the case where permanganate or nitric acid was used as a solvent. With the exception of the stain obtained from the silver solvent a better positive was obtained by this method than in the previous case, since we do not have the jumble effect caused by the negative image. It therefore follows that the negative image is not important in the development of the positive by the Waterhouse process.

In all of the plates obtained with the thiocarbamide developer there was not the usual characteristic black deposit, but a brownish violet color led us to suppose we were dealing with a sulphide. With such a supposition the following solutions were tried as reversing agents, but failure resulted in each case.

All the solutions mentioned below were first tried in the developer and then by a previous immersion, but in no case was there any sign of a reversal taking place The surface was coated with a brown fog when either H_2S or NH_4OH

were used. From this it would seem to follow that there must be some complex reaction in case a sulphide were formed.

No.	Solution	Dilution	Exposure sec.	Type
1	H_2S aqueous	Saturated	1	fogged negative
2	NH_4OH	Normal solution	1	" "
3	H_2S	Sat. diluted $^1/_2$	1	" "
4	H_2S	Sat. diluted $^1/_5$	1	thin fogged negative
5	NH_4OH	N/2 solution	1	fogged negative
6	NH_4OH	N/5 solution	1	negative
7	Urea	5 g in 100 cc H_2O	1	"
8	Urea	1 g in 100 cc H_2O	1	"
9	NH_4CNS	5 g in 100 cc H_2O	1	"
10	NH_4CNS	1 g in 100 cc H_2O	1	"
11	$NH_4OH + H_2S$	Conc. of 1 and 2	1	fogged negative
12	$NH_4OH + H_2S$	Conc. of 4 and 6	1	" "

When a plain negative was immersed in a solution of thiocarbamide no visible reaction was seen to occur. However, when simply silver bromide was treated with the thiocarbamide of sufficient concentration there was an appreciable solvent action, so the reaction must involve some change with the silver bromide. If the thiocarbamide reacted with the decomposed silver bromide in the film yielding a positive because the least exposed parts contained the largest amount of unchanged silver bromide we should obtain a positive by development with thiocarbamide alone provided the exposure was long enough. This was tried and the following results were obtained:

No.	Developer			Exposure	Type
	Thiourea cc	Na_2CO_3 (sol. B) cc	H_2O cc		
1	20	25	20	1 sec.	fogged plate
2	20	25	20	30 sec.	" "
3	20	25	20	1 min.	" "
4	20	25	20	2 min.	" "
5	20	25	20	3 min.	" "

Unless the plate were exposed a sufficient length of time to produce a reduced silver negative there was no appearance of any image. The presence of a developer or depolarizer is essential to the successful operation of the development. However, when a plate is treated in the following developer

No.	Developer			Exposure	Type
	Thiourea cc	Sol. A cc	Sol. B cc		
1	20	25	0	1	slight fog
2	20	25	5	1	partial positive
3	20	25	10	1	" "
4	20	25	25	1	good "

we see that it only requires but a little of the carbonate to increase the reducing power sufficiently to produce an image. It was interesting to note the decided difference in the color of the two completely fogged plates produced in the above two cases, for with only sodium carbonate present we have a light brown fog, but with the hydroquinone and sulphite there is formed a dark brownish purple fog. When two plates were treated in the same manner as the No. 1 in each case and were then fixed, the remaining silver bromide was dissolved off first in every case in the portion corresponding to the shadows.

Some silver bromide was precipitated in the dark and, after complete washing, was treated with the previous thiocarbamide developer. The excess of undecomposed silver bromide was dissolved and after thorough washing the residue was dried. A portion of this was analyzed by precipitation as silver chloride and weighed with the following results:

Wt of original material 0.1701 gram.

Wt of AgCl 0.2236 gram.

Ratio of original material: wt of AgCl = 0.1701 : 0.2236; 0.1701 : 0.2236 = 109.1 : 143.45;

and we see that without any outside reduction by light, we have the final product not in the ratio of silver sulphide, but

of metallic silver; still minor side reactions might form a small amount of sulphide which however is negligible.

This final result showed that the sulphur in the thiocarbamide was not at all essential and that there must be some specific property of the thiocarbamide as a whole. The effect of a thiocarbamide and a regular developer was then tried upon plates exposed the same length of time to the same object and under the same light intensity. For ease in controlling all these details the lecture room, which was illuminated by ordinary electric lights and equipped with very dark window shades, was utilized, and the following exposures were made with this illumination:

No.	Thiocarbamide developer			Regular developer		Exposure	Type
	Thiourea cc	Sol. A cc	Sol. B cc	Sol. A cc	Sol. B cc		
1	20	25	25	—	—	15 min.	good positive
2	0	0	0	25	25	15 min.	thin negative
3	20	25	25	0	0	13 min.	fair positive
4	0	0	0	25	25	13 min.	very thin negative
5	20	25	25	0	0	12 min.	partial positive
6	0	0	0	25	25	12 min.	nothing
7	20	25	25	0	0	10 min.	partial positive
8	0	0	0	25	25	10 min.	nothing

All plates were developed for the same length of time, and all conditions were retained as nearly constant as possible. With the first four numbers the positives were very much more dense than the corresponding negatives. We must then admit that the action of the light was to alter the plate in some manner even at what is considered below the minimum exposure for a negative, but that the regular developer is unable to detect it. As the developer containing the thiocarbamide developed a positive we find that the only way to account for it is by assuming that it develops the undecomposed silver bromide more rapidly than the exposed and in fact all the work upon this developer has pointed towards

this conclusion. When an unexposed plate was treated with the thiocarbamide developer it was found to yield the same brownish violet fog which was so characteristic in the production of positives. The action then becomes very evident, especially since it has been shown that substances which dissolve silver bromide coarsen the grain and hence make a more sensitive plate.[1] As it has been previously pointed out that thiocarbamide does have a solvent action towards silver bromide, we have the unexposed silver bromide made more sensitive to the developer than the exposed and hence the production of a positive on even very short exposures. As a check on this we have the following experiments:

No.	Preliminary immersion		Time of immersion min.	Developer			Exposure	Type
	Thiourea cc	H_2O cc		Sol. A cc	Sol. B cc	KBr cc		
1	20	100	1	25	25	2	15 min.	partial positive
2	20	100	3	25	25	2	15 min.	good positive
3	20	100	5	25	25	2	15 min.	best positive
4	20	100	8	25	25	2	15 min.	positive with thin fog

After the immersion in the thiocarbamide solution the plates were washed for three to five minutes in running water and then developed in the regular developer. The results would then substantiate the theory that we have a sensitizing effect, especially since the thing can be done so successfully in two stages. As a matter of fact, the whole process may be controlled much more satisfactorily by doing it in two stages rather than by simultaneous action. Additional work was carried out to see to what extent the plate could be sensitized. The following results were obtained:

[1] Lüppo-Cramer: Eder's Jahrbuch der Photographie, 21, 368 (1907).

No.	Time of immersion min.	Time of washing min.	Type
1	5	1	fair positive
2	5	1	good positive
3	5	10	partly clouded positive
4	5	20	badly clouded
5	5	30	badly clouded
6	5	5 and dry	clouded plate

The thiocarbamide solution was of the same concentration as in the previous case, as was the developer, and it will be seen that bad results follow if the immersion in the preliminary solution exceeds a certain time. This resultant cloudy effect over the whole plate may be explained by the fact that for too great a period between sensitizing and developing the undecomposed silver bromide in the whole film becomes sensitized as well as perhaps some of the partly exposed and we obtain a more uniform rate of development for both exposed and unexposed bromide. This would seem to be warranted from the behavior of Nos. 2 and 6; for, without drying, a good positive resulted while under the same condition when dried a clouded plate was obtained. From the above data we feel warranted in assuming that the thiocarbamide causes an increase in sensitiveness of the undecomposed silver bromide which is followed by chemical development with a suitable developer.

One disturbing factor to the above conclusions was the work of Kogelmann who obtained negatives with over-exposed plates using the thiocarbamide developer. This process was then taken up and studied with carefully checked plates. The exposures were made out of doors with the camera and were all taken at as nearly the same time as possible. The following is a summary of the results obtained:

No.	Time of exposure min.		Final developer			Type
			Sol. A cc	Sol. B cc	H_2O cc	
1	15	None	25	25	0	good positive
2	15	Yes	25	25	0	good positive
3	15	Yes	25	25	100	fogged negative
4	30	Yes	25	25	0	" "
5	30	None	25	25	0	negative

It will be noticed that under proper conditions only a positive was obtained. Negatives resulted only when there was an over-exposure and an excess of metallic silver was present, or when there was a slight over-exposure and a dilute developer was used. By using an old developer with under-development negatives were always the result. However, if the old developer was allowed to act for a sufficiently long time during development a positive finally resulted. The final conclusions from these experiments were that, with a moderately strong new developer under conditions yielding a positive with regular development, a positive will result with a thiocarbamide developer. This resulted consistently under the conditions of No. 2. An under-development for an over-exposure would yield negatives each time with or without the thiocarbamide immersion. Some additional facts were obtained which still further substantiated the above conclusions. A plate was exposed to solarization similarly to No. 1 and was developed with the ordinary developer. The resulting silver positive was dissolved by means of chromic acid, and the development was continued after a thorough washing in the double thiocarbamide developer with the result that a positive was obtained with a bad surface cloud. Upon the development of a solarized plate we first have the negative image due to the reduced metallic silver appearing and then the positive as obtained under the conditions of regular development, and finally another positive superimposed on the original thin one and due to the sensitizing action of the thiocarbamide. Consequently the resultant

image is not an exceptionally good one, but in any development these stages can be easily watched. When an over-exposure and under-development is given, the amount of reduced silver will mask the positive image and will yield the negative, which is undoubtedly the one previously obtained. Another factor aiding much in the masking by the reduced negative is the heavy surface fog, but several plates which appeared as negatives were treated with chromic acid, and if the action of the acid was discontinued at the proper moment just after the fog on the surface was dissolved, a positive could be seen provided there had not been too great an over-exposure. This positive was the one which would be obtained under the normal conditions of exposure.

When using carefully checked plates to the best solarization, in no case could we obtain a negative with the thiocarbamide solution, if the developer was of the proper concentration and the exposure was correct.

This work was suggested by Professor Bancroft and has been carried out under his supervision.

Cornell University

NEW BOOKS

Müller-Pouillets Lehrbuch der Physik und Meteorologie. *Zehnte umgearbeitete und vermehrte Auflage. Herausgegeben von Leop. Pfaundler. Dritter Band. 17 × 25 cm; pp. xiv + 923. Braunschweig: Friedrich Vieweg und Sohn, 1907. Price: paper, 16 marks; bound, 20 marks.*—"The third volume deals with the phenomena of heat together with the closely related, very important portions of physical chemistry which were formerly classed as molecular physics. As an appendix there is a sketch of meteorology.

"To keep properly in touch with the continuous specializing in science, the editor has secured collaborators: for the chemical-physical matter, a representative of Ostwald's school in the person of Dr. Karl Drucker, privatdocent at Leipzig; for the parts of the theory of heat which require a more rigid mathematical-physical treatment, Professor A. Wassmuth of Graz; for the meteorological appendix Professor Jul. Hann of Vienna after Professor Panter was forced by illness to give up the work."

Pfaundler has written the chapters on thermometry and calorimetry; Drucker those on chemical-physical statics, changes of state, thermochemistry; Wassmuth those on thermodynamics, conduction of heat, and kinetic theory; Hann that on meteorology.

In the chapter on thermometry the author points out, p. 2, that we make the generalization that all substances have the same temperature if there is no mutual change of volume when they are brought in contact, always provided that there is no chemical reaction and that nothing occurs beyond a transference of heat. On p. 39 we find a valuable table for a comparison of the toluene and alcohol thermometers with the hydrogen or air thermometer. On pp. 122–125 are given elaborate tables for the standardization of different types of liquid and gas thermometers. On p. 73 there is the following, very clear paragraph in regard to the apparent expansion of mercury as a measure of the temperature.

"We will now see in how far we are justified in considering the ordinary mercury thermometer as a trustworthy instrument for measuring temperature. If we fill a number of thermometers each with a special liquid, such as mercury, water, alcohol, olive oil, etc., if we then determine for each the melting point of ice and the boiling point of water and if we divide each interval into one hundred parts, we shall find that all the thermometers will agree at 0° and at 100° but that they will differ from each other in general at the intermediate temperatures, a phenomenon first noticed by DeLuc. Thus when the mercury thermometer reads 50°, the water thermometer will read only 25.6°, while the readings on the alcohol and the oil thermometers will be 43.9° and 49° respectively. We will leave the water thermometer out of account because each position between 0° and 9° corresponds to two different temperatures. Of the other liquids there is no one which has an *a priori* right to be considered as a 'more accurate' measurer of temperature than any of the others. It is really quite arbitrary what liquid we select in order to measure temperature by its expansion. Mercury was not chosen 'because it expands regularly with the

temperature;' but chiefly because it does not wet glass, has a low freezing point and a high boiling point. Just so soon as we agree to measure temperature by means of the expansion of mercury, it follows as a result of the definition that the expansion of mercury is proportional to the temperature. In just the same way oil would expand regularly with increasing temperature if we had decided to measure temperature by the expansion of oil. The question which liquid is a more accurate measurer of temperature has no sense until we have an independent definition of temperature, such as the behavior of gases (gas thermometer) or Thomson's scale which we shall discuss later. As a matter of fact, we shall learn that the gas thermometer is for many reasons better than the mercury thermometer as a standard for measuring temperature. One advantage is that the unequal expansion of the glass vessel has much less effect with the gas thermometer."

While the passage just quoted is admirably clear, the following passage, p. 283, leaves one a good deal in doubt as to what the writer really means:

"This fact of the constancy of the contact angle constitutes the second law of capillarity. It must however be noted that experiments do not always confirm this constancy. For instance, the contact angle between glass and water varies, according to Quincke, between 4° and 40° 31′ depending upon whether the glass is as clean as possible or somewhat greasy. The contact angle for mercury also varies between 129° and 143° according to circumstances. There is some reason, however, for believing that the variations are due to very slight changes in the texture of the materials, especially at the surface, and that they would disappear if it were possible to prepare surfaces of absolutely constant texture. If a liquid should wet a solid completely, the contact angle would be zero."

One of the interesting features of the volume is the large amount of space given to the phase rule. On p. 338 we read:

"The great importance of the phase rule justifies its use as a means of classifying and treating all investigations dealing with the state and composition of substances. We did not need it when discussing systems consisting of only one phase but from now on we shall make use of the following classification:"

On p. 404 is the only serious error which the reviewer has noted. In Fig. 287, the pressure-composition diagram for two partially miscible liquids shows a minimum pressure when there are two liquid layers. No such case is known and it certainly does not occur with ether and water, which is the case cited. So far as known, the vapor pressure of two liquid layers is always higher than that of the less volatile component and may be higher than that of either component.

In speaking of Raoult's alleged freezing point constant of 0.062°, the writer seems to be a little hazy both as to theory and fact, for he says, p. 484:

"It appears as though the figure 0.062 is perhaps not correct but with another figure the attempt might be made to get round these variations by taking a different value of M. This assumption is the more probable because a precisely similar table for boiling point constants gives results coinciding remarkably well for a constant having the value of 0.031."

In the section on meteorology, what is said about hail is of especial interest

to the physical chemist and I therefore give rather copious extracts from this part of the book.

"Hail is a frequent accompaniment of thunder-storms. It is generally recognized that, with the exception of fine-grained watery hail, hail falls only during thunder-storms. The electrical discharges are distinctly characteristic; lightning flashes are very frequent, almost incessant, while the thunder is not loud, merely a continuous grumble. The discharges appear to take place only between the clouds and to be of light intensity. In most cases hail falls at the beginning of the storm and the rain comes later. Although the hail begins with the storm, there is not always hail along the whole path of the storm; usually the path of the thunder storm is much broader than that of the hail storm.

"Any attempt to account for the formation of hail must deal chiefly with the answers to two questions. How is it that we get a formation of ice at the warmest season of the year and during the hottest hours of the day? What prevents the hailstones from falling until they have had time, in some cases, to grow to an enormous size?

"The first question is relatively easy to answer in view of our present knowledge in regard to the temperatures prevailing at different levels and to the changes taking place in ascending masses of moist air.

"From ballon ascensions we know that in summer (May to August) the following temperatures prevail at heights of 4 to 10 kilometers even in the hottest hours of the day:

Height in kilometers	4	5	6	7	8	9	10
Mean temperature	—6°	—12°	—18.5°	—26°	—33°	—41°	—47°

"The daily heating extends from the earth only about 1.5 kilometers up into the air. The difference of temperature between the icy upper layers of the air and the highly heated lower layers therefore reaches a maximum in the hot summer afternoons. These observations answer the question as to the source of the cold which can form ice in the air on hot summer afternoons. These cold layers are always to be found at relatively short distances up and it is probable that these distances are even less before and during a hail storm. Barral and Bixis found a temperature of —39° in a rain cloud scarcely 7 kilometers above Paris in July, 1850. On May 13, 1897, the temperatures above Strassburg and Berlin were —21° at a height of 4 kilometers, —32° at 5 kilometers, and —40° at 6 kilometers. The upward sweep of ascending masses of warm air can therefore easily carry them into the icy regions. As a matter of fact measurements show that cumulus clouds and thunder clouds often rise to heights of 8–10 kilometers or even higher. The precipitated water vapor formed at or carried to these heights can therefore consist only of supercooled water or of ice crystals mixed with sleet. It is now easy to see why we get hail chiefly in summer, *i. e.*, in warm air. We have to have heat to carry the air up to the cold regions by giving it the necessary upward sweep, and we have to have a high content of water vapor to furnish the material for a large formation of ice. In winter the vertical temperature gradient is too slight and the air contains too little water vapor; consequently we get no real hail, especially far from the sea.

"There is no especial difficulty in forming a fairly good picture of the way a hailstone is formed. The structure of the hailstone gives us some clues. Round a cloudy, opaque centre, something like sleet, there are transparent shells of ice arranged more or less like the coatings of an onion. These are often full of air bubbles and appear partly white. Trabert has pointed out that a hailstone seems to contain three kinds of ice: the centre of frozen snow; the concentric sheaths of ice; and occasionally clear, even crystalline, ice on the outside, though in very many cases this last form cannot be detected.

"L. Dufour has shown that highly supercooled drops of water are fairly stable; these appear to play an important part in the formation of hail. As soon as they come in contact with needles of ice, they freeze at once, the temperature rising to the freezing point and a small part of the water remaining liquid in consequence of the heat evolved. Grains of sleet form the nuclei on which the ice sheaths are formed from the supercooled drops. Sleet is formed at those levels where the temperature is close to the freezing point and the weather is stormy, as at the surface of the earth in very early spring. Sometimes the frozen masses are covered with ice even then. In summer the isotherm for 0° is higher up and as a matter of fact the precipitation on high mountains during thunder-storms consists chiefly of sleet. The clouds are then much larger and contain more water. Trabert is right in saying that we must look for the formation of sleet where snow crystals and supercooled drops come together, as the structure itself shows. Sleet consists of snow crystals welded together by supercooled drops. Sleet changes to hail when the supercooled drops precipitate in the form of sheaths of ice.[1]

"What takes place in the hailstone from the inside to the outside, takes place also in the clouds from above to below. In the uppermost portions of the clouds we have snow crystals and supercooled drops; in the lowest portions only the ordinary mist at a temperature not much above the freezing point. The upper region furnishes the centre of the hailstone; the middle one the concentric sheaths of ice; and the third the material of the more or less crystalline deposits gradually formed on the hailstone (Trabert). In fact the hailstones often reach the earth while their temperature is far below the freezing point. During the growth of the hailstones the extraordinarily frequent electrical discharges from the hail clouds doubtless play a part and cause a frequent, sudden coalescing of the supercooled drops. Each such coalescing corresponds to a new layer of ice on the sleet grain or hailstone and we thus explain the alternation of transparent and white layers in the sheaths of ice on the hailstone.

"The second question was how the hailstones could remain floating in the air long enough to reach the extraordinary size which they sometimes attain. The only possible explanation for this is that it is due to ascending eddies of air in the hail clouds. It is very probable that hail is formed in vertical, local

[1] On Pike's Peak (4308 m, about 38° N) it has been noticed that the hailstones often consist of snow which has been partly melted and then frozen again, or which has been mixed with drops of water and the mass then frozen. This is evidence that the hailstones must have gone up and down several times and consequently may have passed several times through Hertz's stages of rain, hail, and snow.

eddies of air which move forward with the storm, chiefly along the edge of it. An argument in favor of this is the precipitation of hail over comparatively narrow belts. Such eddies are formed by the sudden uprushing of overheated moist masses of air into the high very cold levels during thunder storms, and also during the general disturbance of atmospheric equilibrium when a cold wind from above passes over the hotter lower layers of the atmosphere. Similar eddies often pass along the surface of contact between hot and cold layers of air, the phenomenon often being repeated a number of times.

"Ferrel considers that hailstones are formed in very violent uprushing eddies of air having small cross-sections, and he assumes that the small hailstones are whirled upward repeatedly until their weight has become so great that they fall to the earth. The velocities called for in the eddies are not improbable ones when we consider the effects produced by local eddies, such as cyclones and tornadoes, even at the earth's surface." *Wilder D. Bancroft*

Dr. I. Frick's Physikalische Technik *oder Anleitung zu Experimentalvortragen sowie zur Selbstherstellung einfacher Demonstrationsapparate. Siebente volkommen umgearbeitete und stark vermehrte Auflage von Dr. Otto Lehmann. Zweiter Band. Erste Abteilung. 18 × 26 cm; pp. xvii + 762. Braunschweig: Friedrich Vieweg und Sohn, 1907. Price: paper, 20; bound, 22 marks.*—As the title itself shows, this book is intended to be of service to the lecturer in physics both by showing just how certain experiments can be performed and also by telling him from what firms he can buy special apparatus for the experiments. The book is eminently successful in both aims. The experiments in this volume are grouped under the headings: electrostatics; galvanism; magnetism; induction. There is an extraordinary number of experiments and they are very well chosen. Some of them are distinctly interesting for reasons other than their merit as lecture experiments. Thus on p. 280 we find the statement that when lead is precipitated electrolytically from an aqueous solution, hexagonal crystals are obtained with a low current density and regular crystals with a higher current density.

There are several experiments on the behavior of isolated conductors in an electrolytic solution through which a current is passing; but they deal chiefly with the special case of no polarization at the surface of the interposed conductor. The reviewer has always liked the experiment of the precipitation of copper from a copper sulphate solution on a detached carbon rod the moment the fall of potential in the solution alongside of the rod exceeds a certain value.

Wilder D. Bancroft

Elementary Agricultural Chemistry. *A Handbook for Junior Agricultural Students and Farmers. By Herbert Ingle. 13 × 20 cm; pp. ix + 250. London: Charles Griffin and Company. Philadelphia: J. B. Lippincott Company, 1908. Price: $1.50 net.*—In the preface the author says:

"This little volume is based upon the writer's long experience in teaching agricultural students, among whom there are, unfortunately, many who cannot devote the time necessary to acquire sufficient knowledge of pure chemistry to profitably read such works as the author's Manual of Agricultural Chemistry.

"It is true that any attempt to combine, in one book, instruction in the principles of general chemistry with the somewhat technical information concerning the chemistry of agriculture, must be in many ways a failure, and the author would strongly recommend the user of this work to read some good, modern text-book on the former; or, better perhaps, to ask his teacher to explain, at greater length, the very incomplete and sketchy accounts which are given of the principles of chemistry and of the properties of the elements and compounds important in agriculture.

"While fully realizing that a satisfactory knowledge of agricultural chemistry cannot be acquired without a previous training in pure chemistry, he is aware that there are many agricultural students and farmers who have, perforce, to do without this preliminary chemical knowledge, and it is for such that this book is mainly intended.

"Since the work is written for the agriculturalist rather than for the chemist, few references to chemical literature are given.

"The book was prepared while the author was in touch with many of the crops and agricultural practices of South Africa, and it was thought advisable to give some account of the products of tropical and sub-tropical agriculture in addition to the matters relating to ordinary English farming.

"In these days of frequent travel and emigration, such inclusions may be of service to many agricultural students who, in the future, may become Colonists, while it may render the book more suitable to the needs of the Colonial reader, and to all a comparison of tropical with temperate conditions, cannot fail to be useful.

"Every writer is apt to give undue prominence to the particular subjects upon which he has himself worked, and perhaps some examples of this weakness may be found in the present volume.

"The importance of the composition as well as the amount of the ash constituents of the food of animals, to which reference is made in chap. ix., though perhaps not strongly felt in Europe where diet is varied, is considerable in such countries as South Africa, where the usual food of draught animals is composed almost entirely of cereals.

"In chap. iii., a brief account is given of the main causes of the motion of water in a soil, intended to clear away the confusion which is apt to attend the usual "explanation" as to its being due to "capillarity."

Chap. x. deals with the variations in the composition of cow's milk in greater detail, perhaps, than the elementary character of the book justifies; but here again the popular interest at present shown in the subject must be the excuse.

"There are doubtless, other respects in which the work is "out of balance," but for these, the reader's indulgence is solicited.

"The author hopes, in spite of this, the book may prove of service to those for whom it is intended." *Wilder D. Bancroft*

Cours de Chimie Inorganique. *By Fréd Swarts. 16 × 25 cm; pp. 706. Paris: A. Hermann, 1908. Price: paper, 15 francs.*—This book is based on the lectures given by the author at the University of Ghent. In some respects, the volume is very much up to date. The Birkeland and Eyde process for making the oxides of nitrogen is described at some length. It is interesting to note

also that free use is made of the theorem of Le Chatelier and of the electrolytic dissociation theory. It is fairly evident that more and more physical chemistry is being introduced in the elementary courses both in Belgium and in America.

On p. 616, the author apparently considers lead acetate purely as a catalytic agent in the conversion of lead into white lead by the Dutch process. According to this view, the white lead is formed by the action of carbon dioxide upon lead hydroxide. If this is the case, it would account for the excellent properties of the white lead made by this process; but it ought also be very easy to duplicate the results by a quicker method. *Wilder D. Bancroft*

Ueber die Schichtungen bei Diffusionen. *Eine Voruntersuchung. By Raphael Ed. Liesegang. 14 × 22 cm; pp. 55. Leipzig: Wilhelm Engelmann, 1907. Price: paper, 1.60 marks.*—The author found great difficulty in repeating his earlier experiments on the ring-shaped deposits of silver chromate formed when silver nitrate is allowed to diffuse into a gelatine film containing potassium bichromate. A long series of experiments finally brought out the fact that the chief variable was the quality of the gelatine. If the gelatine film were allowed to age for several days, marked differences in the arrangement of the rings were obtained. It is not primarily a question of the viscosity of the gelatine, but depends rather on the hydrolytic decomposition of the gelatine. Using the figures as a method of testing, it was found that the gelatine was not the same as a commercial sample of glutine. *Wilder D. Bancroft*

Traité complet d'Analyse chimique *appliquée aux Essais industriels. By J. Post and B. Neumann. Deuxième édition française entièrement refondue. Traduite d'après la troisième édition allemande et augmentée de nombreuses additions par L. Gautier. Tome premier, premier fascicule. Prix, 6 fr. 50.*—The complete work is to consist of two volumes, each having four parts. The present number is the first of volume one. It deals with water, combustibles, pyrometry, and gas. The chapter on pyrometry is the one which will appeal the most to the physical chemist and is an excellent one. In the pages on the optical pyrometers we find a discussion of the instruments of Le Chatelier, Wanner, Féry, Holborn and Kurlbaum (Morse patent). *Wilder D. Bancroft*

Les Rayons Cathodiques. *By P. Villard. (Collection Scientia.) Deuxième Édition. 13 × 20 cm; pp. 107. Paris: Gauthier-Villars, 1908. Price: linen, 2 francs.*—The subject is treated under the headings: apparatus; electrical phenomena in rarefied gases; cathodic emission; electrification of the glass tube; properties of cathode rays; X-rays; electrification of cathode rays; electrostatic effects; action of a magnetic field on cathode rays; velocity of cathode rays; heterogeneity of cathode rays; chemical action of cathode rays; diverse phenomena; formation of cathode rays.

The last two pages of the book are devoted to a discussion of the nature of radiant matter.

"In the first edition of this book we supposed that the cathodic corpuscles were electrified particles of hydrogen. At that time electricity was considered as inseparable from matter and this hypothesis therefore seemed almost necessary, especially as it explained perfectly the reducing action of the rays and the constant presence of hydrogen at the cathode.

"The remarkable work of J. J. Thomson and Max Abraham has shown that the presence of a ponderable carrier for electricity is not necessary and that the laws of electricity are sufficient to explain the chief properties of the cathode rays. Returning to an old hypothesis we assume the existence of electric fluids and, by analogy with ordinary matter, we suppose them formed of atoms of electricity, or electrons, having the absolute value of 1.3×10^{-19} coulomb, which is equal to the charge carried by an atom of hydrogen during electrolysis. Every electrical charge would therefore be composed of a whole number of these elementary indivisible masses and would constitute an exact multiple of the unit charge just mentioned. According to this hypothesis the cathode corpuscles are atoms of negative electricity, in other words negative electrons.

"The inertia of the corpuscles, shown by the form of the trajectories in a field, is to be explained as a phenomenon of self-induction: an electron in motion is equivalent to a current and produces around it a magnetic field, in other words localized energy, the value of which in each space-element is proportional to the volume of the element and to the square of the field. The creation of this energy, *i. e.*, the setting the electron in motion, necessarily requires a certain expenditure of work just as is the case when any ponderable object is set in motion.

"When the motion is once established and provided the velocity is constant, the field produced is invariable and moves with the electron. No expenditure of work is then necessary to maintain the velocity.

"If one stops the electron, the field formed by its displacement will disappear and the energy which this field represents will become free and will tend to prevent the stopping. This energy thus restored is equal to that acquired when the electron was set in motion and is proportional to the square of the field, in other words to the current, and consequently to the square of the velocity just as in the case of the kinetic energy of any material substance.

"These characteristics are precisely those of all mechanical mass and it therefore seems possible to explain ordinary inertia by assuming that matter consists solely of electrons.

"This electromagnetic inertia has one remarkable peculiarity: the mass of an electron increases with the velocity and becomes infinite for the velocity of light. This increase is not appreciable for so-called *mechanical* velocities. It becomes important only as we reach 80 percent of the velocity of light. It has been possible to verify directly this apparent increase in mass by means of measurements made on the β rays of radium, which are true cathode rays but possessing enormous velocities even exceeding the value mentioned.

"The mechanical properties of cathode rays are thus explained in a most simple way. The case of light shows us that it is possible to account for the phenomena of reduction without falling back on hydrogen. Nevertheless there are two difficulties. The β rays of radium color glass and crystal violet and so do the X-rays.[1] The cathode rays from a Crookes tube reduce crystal and it seems difficult to attribute this difference in action merely to a difference in velocity.

"The other difficulty is that the characteristic ratio e/m, of the electric

[1] By oxidation of the manganese.

atom ought to be constant and to appear in all phenomena where we are concerned directly with electrons. As a matter of fact, it varies from 1.865×10^7 (cathode rays) to 3.534×10^7 (Zeeman effect) and even reaches the value of 1.656×10^8 in the crystalline absorption. These discrepancies cannot be explained as due to differences in velocity for these could only increase the value of m and diminish that of the ratio[1] e/m.

"In spite of these anomalies, the electromagnetic theory of the cathodic phenomena constitutes a marked advance, the greatest that has been made in this branch of physics since the work of Sir W. Crookes."

[1] Pellat has recently suggested a very simple explanation of these variations in e/m (Comptes rendus, **145**, 673 (1907)).

Wilder D. Bancroft

Recherches théoriques et expérimentales sur la Constitution des Spectres ultraviolets d'Etincelles oscillantes *By Eugène Néculcéa. 23 × 28 cm; pp. 220. Paris: A. Hermann, 1908. Price: paper, 12 francs.*—This volume contains an account of work begun in 1901. The author summarizes his conclusions as follows:

"The object of this investigation was to study the effect of self-induction on the oscillating discharge with reference to the changes produced in the extreme ultra-violet portion (λ = 2700–2000 Angström units) of the spectra of the metals forming the electrodes between which pass the sparks coming from the discharge of a condenser. At every step there were so many experimental difficulties in the spectrographic study of this invisible region of the spectrum that it has been necessary to devote a portion of this investigation to the theory of spectroscopic instruments based on physical optics, a theory not very familiar to spectroscopists, yet which throws a clear light on a number of apparently obscure points concerning the choice and action of a spectroscopic instrument. As a result of setting forth this theory as doctrine, it is hoped that people will finally give up completely the old views, based on geometrical optics, which are entirely insufficient to give a definite account of the exact way in which a spectroscopic instrument acts.

"We may sum up, as follows, our results on the effect of self-induction on the extreme ultra-violet portion of the spark spectra:

1. Self-induction has a very powerful effect in the extreme ultra-violet region of the spark spectra of the metals we have studied: Tl, Pb, Bi, Sn, Sb, Cu, Ag, Ti, Fe.

2. The different ultra-violet lines of the metals just mentioned can be divided into three groups with reference to the variation of intensity when there is an increase of self-induction in the discharging circuit. The first-class includes those lines which weaken very rapidly with increasing self-induction. The second class includes those lines which only weaken gradually as the self-induction increases. The third class includes the lines whose intensities pass through maxima and minima as the self-induction of the circuit increases. This entirely natural classification of the lines was proposed by Hemsalech for the visible region of the spark spectra. It is also valuable for the ultra-violet portion of the spectrum.

3. These three classes of lines may exist separately in the spectra studied.

As a rule the lines corresponding to the first and second classes are the most common. Lines belonging to the third class are not common in the region we have studied.

4. Lines belonging to the harmonic series of Kayser and Runge never belong to the second class, which is quite contrary to what Hemsalech established in his thesis of 1901; but they often belong to the first and sometimes to the third class.

5. On the other hand the doublets of Rydberg and the triplets of Kayser belong almost exclusively to the second class.

6. We may adopt the following hypothesis in regard to the mechanism of the effect of self-induction on the intensity of the lines. The self-induction modifies the frequency and the intensity of the oscillations of the condenser discharge, with the result that the forced vibrations due to the luminous atoms change and cause the intensification of certain rays or the weakening of others. The capacity will increase the density of the metallic vapor and will probably cause a rise of temperature. Some physicists even believe that they have noticed a modification of the spectra due to this. Our actual knowledge of the luminous emission of a metallic vapor excited by the electric discharge is so incomplete that it is impossible to formulate a sufficiently complete explanation of the effect on the intensity of the spectral lines produced by changes of the electrical conditions in the discharging circuit.

7. We have obtained very interesting results in the ultra-violet portion of the spark spectrum of titanium. We have been able to detect real series of *short lines*, which appear in a very clear manner.

8. This effect of self-induction on the character of spectral lines due to oscillating sparks may serve to indicate in some cases the harmonic relations existing between certain lines of the same spectrum. We therefore have the following methods of studying the character of a line or a series of lines.

(*a*) *Study of Their Appearance.*—We classify the lines as reversed, diffuse, short, etc. This method has already been employed for the reversed lines of palladium and the diffuse lines of copper. Unfortunately the appearance of the lines depends on a number of external circumstances such as the resolving power of the spectroscope, the density and temperature of the metallic vapor, the time which the photographic plates are exposed, etc. The effect of all these things must be taken into account in any such comparison as suggested.

(*b*) *Effect of Temperature.*—There are lines which become more intense or weaker for a given rise of temperature. We distinguish arc lines, spark lines, the enhanced lines of Lockyer, etc.

(*c*) *Effect of Pressure.*—Humphreys and Mohler have shown that pressure has a selective action on the different lines of an element; but their investigations do not cover all the lines of any spectrum.

(*d*) *The Zeeman Phenomenon.*—We investigate the effect of a magnetic field on the different lines of a spectrum.

(*e*) *Crew's Method.*—We study the same spectrum in different gaseous media.

(*f*) *Action of Self-induction.*—Finally, we may employ the method which has been the subject of this investigation." *Wilder D. Bancroft*

THE DIELECTRIC CONSTANTS OF THE HALOGEN HYDRIDES

BY OSCAR C. SCHAEFER AND HERMAN SCHLUNDT

This communication is a continuation of the earlier work of Schlundt[1] on the dielectric constants of pure solvents. The values for the halogen hydrides—hydrogen iodide, hydrogen bromide, and hydrogen chloride—in the liquid state, are now added, and the value of solid hydrogen cyanide is included, the dielectric constant of the liquid having been published some years ago.

The dielectric capacity of the halogen hydrides is of interest at this time in connection with the researches of Steele, McIntosh, and Archibald[2] on the physical constants, solvent, and ionizing power of these compounds. The subsequent work of Archibald[3] revealed the fact that these solvents yield excellent conducting solutions with several organic acids and alcohols. On the basis of the Nernst-Thomson rule, that a close parallelism exists between ionizing power and dielectric capacity, one would be inclined to assign medium or high values to the dielectric constants of these solvents. The results obtained, however, show that the halogen hydrides fall in the class of solvents having low dielectric capacity of which ether and chloroform may be taken as examples.

Preparation of Compounds.—In the preparation of the hydrides studied, stress was laid on securing pure samples of the compounds in the liquid state. The final measurements were conducted with samples that had been redistilled. Precautions were taken to exclude moisture, and some of the measurements were repeated because traces of water were detected in the samples used. In this connection we found that samples known to contain a small quantity of water gave

[1] Jour. Phys. Chem., **5**, 157, 503 (1901); **8**, 122 (1904).
[2] Phil. Trans., 205A, 99 (1906).
[3] Jour. Am. Chem. Soc., **29**, 665, 1416 (1907).

values for the dielectric constant that exceeded those of the pure solvents by only about 1 percent—a difference almost within the limits of measurement. In the case of hydrogen chloride, a sample containing water in small quantity, when cooled in a bath of solid carbon dioxide and ether, soon shows minute, white flakes of ice or a hydrate. Evidently the solubility of ice in liquid hydrogen chloride is very limited at low temperatures. We also noted that traces of bromine in liquid hydrogen bromide, or iodine in liquid hydrogen iodide, cause practically no change in the value of the dielectric constant.

Liquid hydrogen iodide was prepared by dropping water from a tap funnel on a warmed mixture of red phosphorus (one part) and iodine (ten parts) contained in a generating flask supplied with a manometer tube dipping into mercury. The evolved gas was passed through a series of large U-tubes—two containing glass beads moistened with concentrated hydriodic acid, and two containing fused calcium chloride, before it was condensed in a small receiver cooled in a bath of solid carbon dioxide and ether contained in a Dewar tube. The outlet tube of the receiver was protected from atmospheric moisture by a calcium chloride tube which was in series with a water suction pump. The whole apparatus was exhausted to a pressure of 2 cm before the generation of the hydrogen iodide was started. The condensed product was generally colored by a trace of iodine. A colorless sample was obtained by distilling the liquid again and condensing the vapor directly in the measuring cells. Finally the arms of the cells were sealed off in a small flame at constricted points.

For the preparation of liquid hydrogen bromide, an apparatus similar to the one just described was charged with moistened red phosphorus, and bromine was added from the drop funnel. Bromine vapors were removed by passing the gas through a U tube charged with moist red phosphorus, and a second tube containing glass beads moistened with concentrated hydrobromic acid. The condensed liquid was further purified by distillation.

To liquefy hydrogen chloride, the temperature of Thilorier's mixture was reduced to —100° C. by evaporating the carbon dioxide under low pressure. Hydrogen chloride was generated by allowing concentrated sulphuric acid to drip on common salt in the usual form of apparatus. The gas was dried by passing it through concentrated sulphuric acid and calcium chloride, and the liquid was finally redistilled.[1]

Measurements.—The dielectric constants were determined with the well known apparatus devised by Drude. The improved apparatus of Schmidt[2] was used. As the measurements were extended to room temperatures, special forms of cells had to be constructed for confining the liquids. By fusing a side tube on to the usual form, at a point close to the bulb, a very serviceable cell was obtained. Another form consisted of a small U tube, slightly widened at the bend where the platinum plates were sealed in. The cells were calibrated with the standard solutions of acetone and benzene recommended by Drude. At least two independent determinations were conducted with different samples of each of the liquids in cells whose dielectric capacity differed somewhat.

DIELECTRIC CONSTANTS OF HALOGEN HYDRIDES

Substance	D. C.	Temperature	Temperature coefficient
Hydrogen iodide	2.90	21.7	—
Hydrogen iodide	2.88	—50	zero
Hydrogen iodide (solid)	3.95	—70	—
Hydrogen bromide	3.82	24.7	—0.6%
Hydrogen bromide	6.29	—80	—
Hydrogen chloride	4.60	27.7	—0.8%
Hydrogen chloride	8.85	—90	—
Hydrogen cyanide (solid)	2.4	—25	—0.6%
Hydrogen cyanide (solid)	3.05	—70	—

[1] Further details of preparation and figures of the apparatus used are given by Oscar C. Schaefer in his thesis for the degree of Bachelor of Science, University of Missouri, June, 1909.

[2] Drude's Ann., 9, 919 (1902).

Results.—The values given for the dielectric constants in the table, unless otherwise indicated, refer to the substances in the liquid state under their own vapor pressure at the temperature given.

Comparing the values obtained at room temperatures, it is seen that the dielectric constants increase with decrease in molecular weight. Hydrogen iodide excepted, the temperature coefficients are negative. Hydrogen iodide shows an increase in dielectric capacity upon solidification. Hydrogen cyanide, on the other hand, shows a great fall, the value in the liquid state being about 100.

The dielectric capacity of the halogen hydrides is low in comparison with solvents that possess marked ionizing power, such as water, formic acid, the nitriles, and liquid sulphur dioxide. Their marked ionizing power is therefore somewhat anomalous. Unless we assume abnormally high values for the mobilities of the ions in the solutions of the halogen hydrides that Archibald[1] found to be excellent electrolytes, we are forced to the conclusion that other factors besides the dielectric constant must be considered in estimating the ionizing power of solvents.

Chemical Laboratory,
University of Missouri

[1] Loc. cit.

BASIC MAGNESIUM CHLORIDES[1]

BY W. O. ROBINSON AND W. H. WAGGAMAN

Sorel[2] describes a cement made by mixing calcined magnesia with a concentrated solution of magnesium chloride. This material much resembled marble and was used in mosaics with beautiful effect. When mixed with other material its "flocculating power" was so great that three or four times its weight of foreign material could be used. Sorel states that this cementing material was not affected by water, a statement which later workers have shown to be incorrect.

Bender[3] prepared a basic magnesium chloride by a method similar to that of Sorel's. The magnesia usta of commerce was ignited and over this was poured a strong solution of magnesium chloride. This material was dried in air for six months, then analyzed. Different portions contained different amounts of magnesium carbonates, resulting from the absorption of carbon dioxide from the air. Bender assumed that all the carbon dioxide was combined with the magnesia to form normal, anhydrous, magnesium carbonate, and by deducting the requisite amount of magnesia corresponding to the carbon dioxide content, he found the substance to be represented by the formula

$$5MgO.MgCl_2.17H_2O.$$

His analyses agreed poorly and the molecular ratio of the average was about 5½ : 1.

Davis[4] found fine needle-like crystals which had deposited in mass on the bottom and sides of a reagent bottle containing magnesium ammonium chloride with an excess of ammonia. The material was divided into two parts, A and B. A was washed with a small amount of cold water until

[1] Published by permission of the Secretary of Agriculture.
[2] Comptes rendus, 65, 102 (1867).
[3] Liebig's Ann., 159, 341 (1871).
[4] Chem. News, 25, 258 (1872).

free from ammonium salts. The analyses showed the composition of this residue to be $5MgO.MgCl_2.13H_2O$. B was washed with a much larger quantity of water for several days. It contained no chlorine and the ratio of magnesia to water was between $MgO.H_2O$ and $4MgO.5H_2O$.

Krause[1] claimed that Bender's[2] analyses were not accurate, for the basic residue was allowed to stand in air until carbon dioxide had been absorbed, and that the assumption that the carbon dioxide had combined to form a normal anhydrous carbonate was improbable, for with such an excess of base, a basic carbonate would have formed.

Krause prepared his oxychloride by shaking up magnesium oxide in a solution containing a large excess of magnesium chloride, and heating and cooling with intermittent shaking until nothing but acicular crystals could be observed with the aid of the microscope. The mother liquor was then decanted off and the residue washed with water until only an opalescence was observed by the silver nitrate test. An analysis of the material dried at 110° showed:

$$10MgO.MgCl_2.14H_2O.$$

André[3] formed a basic magnesium chloride by adding 20 grams of calcined magnesium oxide to a boiling mixture of 500 grams water and 400 grams crystallized magnesium chloride. The analysis of the solid residue gave the molecular ratios indicated by the following formula:

$$MgO.MgCl_2.16H_2O.$$

André states that the crystals immediately decomposed on washing with water or alcohol. It is probable that André analyzed a mixture of mother liquor and basic magnesium chloride.

Since basic magnesium chloride is decomposed by washing, it is evident that the previous analyses have been made

[1] Liebig's Ann., **165**, 38 (1873).
[2] Loc. cit.
[3] Comptes rendus, **94**, 444 (1882).

on decomposed material, or as in André's case on a salt contaminated by mother liquor.

It has seemed that the composition of the basic magnesium chlorides and the ranges of concentration of solution over which they can exist could best be determined by a study of the solubility of magnesium hydroxide in solution of magnesium chloride of various concentrations. The 25° isotherm has been determined.

The magnesium chloride ($MgCl_2.6H_2O$) used in the research was found to contain no impurity other than a very slight trace of calcium. The magnesium oxide was prepared from this sample by precipitating with ammonia and washing. It was then strongly ignited, pulverized, and put in containers protected from the air.

Twenty bottles were made up in regular steps of concentration from pure water to a saturated solution of magnesium chloride. A small amount (1 gram to 200 cc solution) of magnesium oxide was then added and the bottles were placed in a thermostat where they were subjected to constant shaking. It was noticed that the residue tended to collect in lumps. These were broken down from time to time. At the end of six months the residues had become homogeneous, and analyses of the solutions from several bottles at intervals of two months, showed no change in concentration. By means of a microscopic examination it was found that the residue of the dilute solutions were kernel-like and amorphous, while the residues in the concentrated solution were composed of very fine, acicular crystals.

The bottles were allowed to settle and the clear solution drawn off and analyzed for magnesium and chlorine. They were also titrated against standard hydrochloric acid N/50, using phenolphthalein as indicator. On account of the small amounts present the determinations are necessarily poor. They are given in Table I, and when plotted show two distinct curves.

TABLE I

Showing the solubility of MgO in solutions of $MgCl_2$ at 25°

Percent $MgCl_2$	Percent MgO as $Mg(OH)_2$
2.36	0.00008
4.47	0.00028
6.79	0.00048
9.02	0.00080
13.14	0.00115
15.15	0.00195
17.53	0.00240
18.52	0.00250
22.04	0.00245
23.78	0.00235
25.13	0.00230
26.88	0.00250
28.34	0.00230
29.80	0.00240
30.04	0.00250
34.22	0.0030

TABLE II

Serial No.	Solution			Residue		Solid phase
	Sp. gr.	Percent MgO	Percent HCl	Percent MgO	Percent HCl	
1	1.019	0.99	1.77	41.56	0.99	Indefinite solid solution
2	1.038	2.02	3.85	12.90	2.91	" " "
3	1.056	2.88	5.16	19.21	4.00	" " "
4	1.075	3.82	6.80	17.17	5.20	" " "
5	1.111	5.57	9.94	19.95	7.67	" " "
6	1.129	6.42	11.52	15.86	9.86	" " "
7	1.141	7.13	12.76	22.74	14.88	$2MgO.HCl.5H_2O$
8	1.162	7.85	14.17	23.71	15.70	"
9	1.192	9.34	16.51	22.01	16.98	"
10	1.209	10.08	17.83	22.59	17.63	"
11	1.226	10.65	19.16	24.40	18.24	"
12	1.245	11.39	20.68	24.91	18.93	"
13	1.256	12.01	21.53	23.80	19.69	"
14	1.274	12.63	22.73	25.64	19.95	"
15	1.282	13.24	23.92	26.38	20.18	"
16	1.302	13.86	24.58	—	—	"
17[1]	1.321	14.49	26.05	25.50	21.80	"
18[1]	1.345	15.19	27.38	—	—	$MgCl_2.6H_2O$

[1] Represents a saturated solution of $MgCl_2.6H_2O$. Concentration 55.76 grams anhydrous $MgCl_2$ to 100 grams H_2O.

The residues were sucked as completely as possible from the mother liquor, but not washed at all, and analyzed for magnesia and chlorine. The results are given in Table II. When plotted on the triangular diagram shown in Fig. 1 it is plain that an indefinite solid solution of magnesia-chlorine and water exists up to a concentration of about 10 grams $MgCl_2$ to 100 cc solution, and that beyond this concentration up to a saturated solution of magnesium chloride there exists a basic magnesium chloride of definite composition.

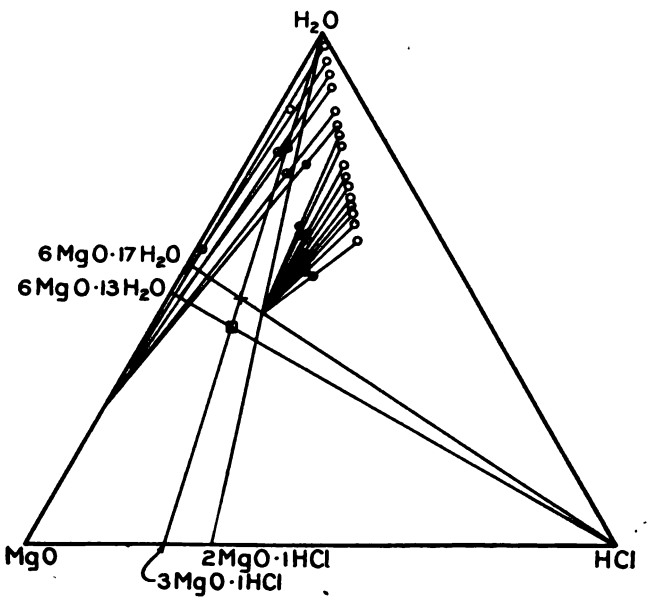

Fig. 1

This solid, by scaling off on the triangular diagram, was found to consist of

$$2.02MgO.1HCl.5.04H_2O \text{ or } 3MgO.MgCl_2.10H_2O.$$

In this paper a study of the system magnesia (MgO), hydrochloric acid (HCl) and water (H_2O) at 25° with the

MgO in excess has been outlined. A hitherto undescribed basic magnesium chloride of definite composition has been identified and the limits of concentration of aqueous solution over which it is stable as solid phase have been determined.

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A KINETIC INTERPRETATION OF OSMOTIC PRESSURE

BY M. M. GARVER

In the modern theory of dilute solutions, what is known as osmotic pressure plays a very prominent part, a fundamental assumption with some writers being that the observed pressure is due to an "expansive force" of the dissolved substance exerting a pressure analogous to that of a gas, or, as other writers put it, "a dissolved substance in solution 'obeys' the gas laws." Notwithstanding the very great success of the theory in explaining phenomena and in furnishing a basis for deducing numerical relations by assuming that the numerical values of the general gas equation apply to the dissolved substance in dilute solutions, some writers are careful to state that their deductions are entirely independent of any hypothesis as to the cause of the observed pressure. This indicates that the gas analogy hypothesis does not satisfy their minds—that there is a lack of physical verisimilitude in the hypothesis, although the numerical relations based on experience are accepted as being beyond dispute. If the function of a scientific explanation of a physical phenomenon is to exhibit to the mind the mechanical relations of the various elements of the phenomenon, then it must be admitted that there is a gap in the current explanation of "osmotic pressure" that many minds are unable to bridge. This sometimes leads to actually grotesque or absurd statements in some of the text-books. A satisfactory mechanical explanation of the osmotic process entirely free from arbitrarily assumed "forces" and "tendencies," and that is at the same time consistent with all the known facts, has apparently not yet been developed. Scientifically considered, the interpretation of a phenomenon is often quite as important as the establishment of the existence of the phenomenon itself.

If we examine the two leading hypotheses at present

current we shall find that besides being philosophically weak, they fail entirely to explain, and are inconsistent with, certain other well-established experimental facts. By the "two leading hypotheses" I mean, first, that the external work done by the osmotic cell, or other device using a semi-permeable wall, is due to an expansive force exerted by the dissolved substance 'tending' to occupy a greater volume, and secondly, the alternative hypothesis that the increase in volume and consequent increase in pressure observed in osmotic experiments are due to some kind of attractive force exerted between the molecules of solute and solvent. Both hypotheses can be shown to be untenable. If then, all attempts at explanation based on these two hypotheses are definitely and distinctly eliminated as being untenable, we are free to re-examine the subject with a view to finding some hypothesis that *is* tenable.

We know from thermodynamics that the external work which may be done by a substance in passing *from* the state A *to* the state B, is a maximum when the process is reversible and is the same for all reversible processes between the same two states, the result depending only on the initial and final states. Therefore, if we dilute a solution isothermally and reversibly from the state A to the state B, the external work done will depend only upon the initial and final states. For the details of such a process, using a semipermeable piston and "explained" in terms of the "expansive force" of the dissolved substance, the reader is referred to the text-books.[1] An equal amount of external work may, however, be done by an entirely different process, using a different device, working isothermally and reversibly between any two chosen states of dilution, where neither an expansive force of the dissolved substance nor any specific attractive forces of any kind between the solute and solvent, other than those which come into play during ordinary condensation and vaporiza-

[1] See Nernst, "Theoretical Chemistry," translated from the 4th German edition, pp. 130–131.

tion, can be admitted as taking any part whatever in the production of the external work.

The experimental fact that the saturated vapor of a dilute solution of a non-volatile solid in a liquid solvent exerts less pressure than the saturated vapor of the pure solvent at the same temperature may be utilized to carry out a reversible isothermal process between any two given states of dilution. By the thermodynamic principle just stated the amount of external work done must be the same in the two cases, since both are reversible; therefore, the ultimate source of the work done must be the same in both; at least, any hypothesis worth considering must include both. Philosophically it would be absurd to invent separate hypotheses for each separate case.

If two vessels, both containing the same liquid, one of which in addition, contains a foreign solid substance in solution, be placed side by side in a space from which the air is exhausted, isothermal distillation will take place, the volume of the solution increasing at the expense of the volume of the pure solvent. Now suppose that instead of placing them side by side, that the solution of strength A be placed on a shelf at a height h_1 centimeters above the level of the pure solvent. To insure equalization of temperatures, suppose both vessels to be put in thermal contact with the same good conductor of heat. Over all place a cover and exhaust the air. The height h_1 may be so chosen that the vapor of the solution A will be in kinetic equilibrium with the vapor of the pure solvent at that height. There will then be no change of volume of the solution. Now suppose that at the height h_2 the vapor of the solution of strength B will be in equilibrium with the vapor of the pure solvent at that height where $h_2 < h_1$ and B is more dilute than A. By slowly changing the elevation of the solution—so slowly that its vapor may be regarded as always in equilibrium with the surrounding vapor of the pure solvent—the degree of dilution may be increased or decreased at will between any chosen degrees of dilution. Here we have a reversible isothermal process, the work done

between the two limits h_1 and h_2 being evidently $g \int_{h_1}^{h_2} h \, d \, m$ where dm represents the increment of the mass of solvent at the height h, and may be either positive or negative. If we express mass in terms of volume and density we will have

$$W = \rho \, g \int_{h_1}^{h_2} h \, dv.$$

If v be expressed as a function of h, the work done on or by the solution between the limits may be determined, but the important point to observe, is, that *the work is independent of any force function whatever*, except gravity, and that may be included as a constant.

By the first law of thermodynamics, heat must disappear when mechanical work is done. In the above ideal experiment, the heat equivalent of the external work done, it may be seen, will come from the cooling of the vapor of the pure solvent, if it expand isentropically, or from the environment, if the expansion be isothermal. In either case no work is done by the expanding solute any more than if additional liquid solvent were added directly by hand. In the osmotic cell the heat equivalent of the work done is assumed to come from the cooling of the expanding solute acting like a gas! But since the dissolved substance could not be cooled without cooling the surrounding solvent the solution, if the supposition be correct, must be *cooled* when mechanical work is done unless heat be supplied by the surroundings. By reference to the above experiment it is seen that the solution would be *warmed* by the condensing vapor while doing mechanical work, were it not in thermal communication with the pure solvent. However, the important point is, that since the same amount of work may be done in passing between two identical states by two different processes, in one of which it is evident that no expansive force, or attractive forces of any kind can have been the active cause, the hypothetical forces become unnecessary complications and explain nothing.

But, moreover, other experiments show that the osmotic pressure is numerically equal to the pressure due to an equal number of gas molecules occupying the same volume at the same temperature as the solute. Hence if the increase of volume of solution be attributed to an attractive force of any kind acting between the molecules of solute and solvent, the hypothesis that the observed resistance to filtration is due to the bombarding molecules of the dissolved substance must be abandoned, since the resistance to filtration would necessarily be the sum of the two actions. Hence the simplest hypothesis is that the attractive forces are negligibly small. This conclusion accords with that previously drawn from the results of the isothermal distillation experiment.

It is just at this point that misinterpretation has crept in. The admission that the resistance to filtration is numerically equal to the pressure required to confine a gas having an equal number of molecules at the same temperature in the same volume as the dissolved substance does not by any means imply that the dissolved substance "tends to expand like a gas." This view is introduced surreptitiously, as it were, by the statement that the osmotic pressure "obeys" the gas laws. Numerical equality of certain relations does not warrant the use of the word "obey." Just here is the gap that requires bridging. No one who accepts Pascal's principle as a physical law can realize in thought just how, mechanically, an "expansive force," under the given conditions, can produce a seemingly negative pressure; hence the mind remains unsatisfied.

This mechanical difficulty may be overcome if one can mentally realize just what takes place during isothermal distillation. The vapor of the pure solvent has a greater density and consequently exerts a greater pressure at the same temperature than is exerted by the vapor of the same solvent when a foreign solid substance is held in solution. Hence when a solution and the pure solvent of the same solution are side by side at the same temperature, there results a transfer of material from the pure solvent to the solution with

corresponding changes in volume. The mechanical paradox of the osmotic cell disappears entirely if we imagine the interstices of the cell-wall to be *occupied only by the vapor of the solvent.* Isothermal distillation then takes place through the cell-wall with a corresponding increase in the volume of the solution, until balanced by a pressure that forces the pure solvent out of the solution into the interstices of the cell-wall, *i. e.*, until the filtration pressure is reached. Under these latter circumstances, as much solvent will leave as enters the cell. If this be admitted, merely as a provisional hypothesis, all paradoxes and mechanical difficulties disappear. It would be a simple explanation *if true.*

Now if we can explain isothermal distillation mechanically, and show that the result must be the same whether the interstices be regarded as filled with either the liquid or vapor, we shall have the clue to the mechanism of the osmotic cell.

It has been somewhere well stated that the study of osmotic phenomena has given a wonderful impulse to the kinetic theory. If this be so, it is highly probable that the phenomena of osmosis are explicable only in terms of kinetic phenomena. This latter statement seems to apply particularly to the doing of work by means of isothermal distillation, where no evidence of active forces is traceable. It seems but fitting, therefore, that we should seek to explain by means of the kinetic theory the phenomena of the osmotic cell. Hence, with a view to bringing them immediately under the eye, the statement of a few of the deductions from the molecular kinetic theory, which if admitted will enable us to understand the mechanism of the osmotic cell, may here be permitted. Without going into any detail, a few of the generally accepted deductions which have a bearing on isothermal distillation and kindred phenomena may be stated.

1. The mean kinetic energy of translation of a molecule depends upon its temperature and is the same for liquids and vapors at the same temperature.

2. The energy of translation of individual molecules in

liquids and vapors varies between zero and some upper limit depending upon circumstances.

3. In the absence of chemical action, a gaseous mixture of different molecules of unequal masses, at the same temperature, tends toward a state having the same average energy of translation per molecule.

4. The vapor of a liquid is composed of those molecules, favorably situated, possessing sufficient energy of translation to enable them to escape through the non-homogeneous surface layer of the liquid.

5. All cases of chemical equilibrium are kinetic, *i. e.*, reaction balancing action.

Let us apply these deductions to dilute solutions. To fix the ideas let us take the case of a non-saline solution such as an aqueous solution of sugar. The molecule of sugar is 19 times as heavy as the normal water molecule; hence will have in solution an average velocity lying between one-fourth and one-fifth that of the normal vapor of water molecule. We shall find that, in general, the molecule of solid solute is heavier than that of the liquid solvent and will consequently possess a lower mean velocity of translation than the molecules of the solvent. Moreover, when a solid is dissolved in a liquid without producing chemical action or appreciable change of volume, there is a fall in temperature indicating that the solvent has given up energy to the solid in the process of changing the solid to the liquid state. It is evident that the average molecular energy of translation of the solvent has been lowered while that of the solid has been raised. The transferred energy could come only from those molecules of the solvent having more than the final average energy, so that the average of those having an excess of energy will be lowered *more than the general average is lowered.* If now, by the application of heat, the original temperature be restored, the original average molecular energy of translation will be restored, but not the original distribution of molecular energy. Since the mean of the energy of one-half of the molecules is lowered without dis-

turbing the mean of the whole, the mean of the other half must be raised proportionately. The net effect is that the foreign molecule acts as though it were a carrier of energy from those molecules having an excess of energy to those having less than the average, with the result that, in a solution, the molecular energy is concentrated more closely about the mean molecular energy than is the case with the liquid pure solvent.

These considerations suggest a simple hypothesis which will enable us to understand and explain many of the phenomena connected with solutions. Let us suppose that in a solution the presence of a foreign non-volatile molecule has the effect of narrowing the range of the velocities of the lighter molecules of the solvent, so that while the average molecular energy of translation will depend upon the absolute temperature, there will be fewer molecules in a solution than in the normal pure solvent, possessing either exceptionally high or exceptionally low velocities.

It should be noticed particularly that the foreign substance is supposed to possess an average molecular *energy* of translation (not velocity) equal to that of the solvent; consequently the disturbing effect of the dissolved substance should be proportional to the *number* of molecules rather than to their mass, since the energy per molecule is independent of the mass.

This hypothesis, if accepted, will be found to enable us to explain many phenomena that are now obscure, such as:

The depressed vapor tension of solutions with accompanying elevation of boiling point and lowering of the freezing point.

Landsberger's method of determining boiling points of solutions.

Isothermal distillation.

The osmotic cell.

Hydro-diffusion.

These are all closely related phenomena and all should be explainable in terms of something they possess in common, *i. e.*, by a single hypothesis.

Let us apply the hypothesis first to the depressed vapor tension of solutions.

It appears from the kinetic theory of solutions[1] that the non-homogeneous surface layer of a solution is free from the dissolved substance, while throughout the rest of the solution the dissolved substance is uniformly distributed. In that case, the absorbing power of the surface of the liquid solution for its vapor will be the same, at the same temperature, as a surface of the pure solvent, and, by Henry's law, will be proportional to the pressure of the vapor upon it. Since kinetic equilibrium ensues when as many molecules return to the liquid as leave it, the reduced vapor pressure of a solution indicates that fewer molecules will be returned to the liquid than in the case of the pure solvent. Therefore fewer molecules must have had sufficient energy to make their way out through the surface layer—a result evidently in accordance with the hypothesis.

The elevation of the boiling points and the depression of the freezing points of solutions may be taken as a measure of the degree of concentration of the molecular energies of the solvents about a mean energy, or, as we may put it, indicate the degree of narrowing of the range of molecular velocities. This may be best shown, perhaps, by first considering the relation of these points to the normal liquid solvent.

The boiling point of a normal pure solvent is that temperature at which the vapor in contact with the liquid exerts a pressure of one normal atmosphere. By the hypothesis, this temperature should be *higher for a solution* than for the pure solvent, for a higher temperature is required in order to give the necessary energy to a sufficient number of molecules to enable them to escape through the non-homogeneous surface layer, *i. e.*, the boiling point of a solution should be raised.

As to the freezing point of the pure solvent, the liquid

[1] Boynton, "Kinetic Theory," p. 221. In the same work will be found references to the original papers warranting the above statements.

must commence to solidify when the molecules of *least* energy take the solid form, keeping the temperature constant by giving out their heat of liquefaction until all are solidified.

By the hypothesis, in the case of a solution, the lower range of molecular energy is *raised* nearer the mean; consequently a *lower* temperature would be required before any of the molecules took the solid form, after which the process would proceed as with the pure solvent, *i. e.*, the freezing points of solutions of solids should be lowered.

The fact that a solution may be boiled by passing into it the vapor of the pure solvent, although the boiling point of the solution may be considerably higher than the temperature of the entering vapor, is a standing paradox that I have never seen even an attempt to explain, although the experimental fact is utilized in Landsberger's method of determining boiling points. If, as the hypothesis supposes, the foreign molecule absorbs energy readily from those molecules of the solvent having energy above the average, then the solution will absorb energy from the inflowing vapor until the solution gives off as much energy as it receives, *i. e.*, boils, although the temperature of the solution is higher than the *average molecular* temperature of the inflowing vapor. In order that the temperature should continue to rise it is merely necessary that the heat given out by the *absorbed and condensed* portion of the vapor should exceed the heat carried away by the unabsorbed and *uncondensed* portion of the inflowing vapor.

The mechanism of isothermal distillation will be readily understood from the previous explanation of depressed vapor tension. The two surfaces, those of the pure solvent and of the solution, have equal absorbing power at the same temperatures, but the solution furnishes less vapor than the pure solvent. Therefore the surface of the solution will absorb more than it supplies, or the volume of the solution must increase in the presence of saturated vapor from the pure solvent.

To apply the hypothesis to the osmotic cell we simply

have to remember that although the average molecular energy of translation is the same for both the external pure solvent and the interior solution, a larger proportion of the molecules of the solvent than of the solution possesses exceptionally high velocities and energies. This fact is shown by the more copious vapor of the pure solvent. Hence if the interstices of the cell-wall are filled with vapor of the pure solvent having a pressure higher than the vapor pressure, due to the solution, condensation will take place where the vapor touches the solution, so that the volume of the solution will increase. This will continue so long as there is any break in the continuity of the liquid in the interstices. But suppose the external pure liquid solvent actually penetrates and touches the interior liquid solution. The only effect of this contact will be to remove the non-homogeneous surface layer, allowing even freer play to the molecules of the pure solvent. They can then pass directly into the solution at the point of contact without giving up a portion of their energy to the superficial layer. In the solution, they soon lose their exceptional energy, so that not as many molecules will be able to find their way out as in, unless aided by an interior hydrostatic pressure. Equilibrium, or the maximum pressure, will be reached when as many molecules pass out as in, and this maximum pressure is evidently the pressure necessary to separate by filtration the solute from the solvent.

The Mechanism of Diffusion.—If the effect of the presence of a dissolved substance in solution is to diminish the normal wide range of the molecular activity of the solvent, it is at once apparent that diffusion of the dissolved substance throughout the liquid is quite a different process from that ordinarily supposed. The dissolved substance would "tend to become uniformly distributed," not on account of any inherent activity in the dissolved substance itself, but because at every point where there was a difference in degree of dilution, the more active molecules of the solvent would make their way into the denser solution faster than the molecules already in the solution could make their way out. This

view, moreover, accords better with the generally accepted doctrine that molecular activity is the greater in the lighter molecule. If the energy of a molecule is independent of its mass, then molecules must have velocities inversely proportional to the square root of their masses. Since, in general, the dissolved solid will have a greater molecular weight than the liquid solvent, it is running counter to all accepted molecular theory to endow the heavy molecule in a mixture with special and unusual activity. It will be found that to transfer the activity from the solute to the liquid solvent will accord just as well with the experimental facts of diffusion. Take Fick's law, for instance. From the fact that the difference in vapor pressures is proportional to the difference in concentration, and the difference in vapor pressures represents the differences in activity of the solvent as modified by the foreign substance, the proposed hypothesis seems in no way in opposition to the observed facts. From the observed vapor pressures, it is evident that, in a solution possessing uniform temperature, no permanent state of equilibrium is possible except a uniform distribution of the dissolved substance.

State College, Pa.,
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THE PHOSPHORESCENCE OF SOME INORGANIC SALTS

BY JOHN ANDERSON WILKINSON

That there is some relation between phosphorescence or fluorescence and chemical action has been shown in a number of cases.

The phosphorescence of phosphorus has been known to be due to oxidation for some time and Ewan[1] has shown the relation between the phosphorescence and the pressure of the oxygen, the limits of the former depending upon the latter.[2]

The phosphorescence and fluorescence of the salts of quinine have been shown to be due to hydration and dehydration. Kalähne[3] and Le Bon[4] have shown that if quinine sulphate is heated suddenly, above 100°, there is a faint phosphorescence which lasts for only a short time. On cooling, the same thing can be seen. If the salt is allowed to cool in the absence of water vapor no luminescence is observed. This shows that the hydration and dehydration of the salt give out light.

Miss Gates[5] worked on the ionization of gases and on the change of conductivity caused by quinine sulphate when phosphorescing as a result of heating. She showed that the light is due to a change in the molecule and not to its giving off charged particles as a radioactive body does. This agrees with Le Bon's experiments.

Villard,[6] in his work with the X-rays, found that the cathode rays turned glass black, due to the setting free of lead. If the cathode rays are cut off by a piece of aluminum which is transparent to the X-rays but not to the cathode

[1] Ewan: Zeit. phys. Chem., **16**, 315 (1898).
[2] Corne: Jour. pharm. Chim. [5], **6**, 17.
[3] Kalähne: Drude's Ann., **18**, 450 (1905).
[4] Le Bon: Comptes rendus, **130**, 891 (1900)
[5] Gates: Phys. Rev., **19**, 135 (1904).
[6] Villard: Comptes rendus, **129**, 882 (1899).

rays, the glass is turned violet. This, he says, is due to the presence of manganese in the glass. P. Curie and Sklodowski Curie[1] found that ozone was to be detected in glass vessels containing radioactive salts and that these salts affect the glass, turning it deep violet, especially where the salt is in contact with the glass. This is true even when the glass contains no lead.

Barium platinocyanide turns dark under continued exposure to excitation but regains its original color when exposed to sunlight.

Wiedemann and Schmidt[2] have investigated the fluorescence, phosphorescence and thermo-phosphorescence of a large number of simple salts and solid solutions in the cathode rays. They divide the simple salts into three groups.

I. Those which show fluorescence and phosphorescence and also decomposition under influence of cathode rays.

II. Those which show fluorescence and phosphorescence but no apparent decomposition.

III. Those which show no luminescence.

Under the first group are placed the halogen salts of the alkali metals, silver, mercury and lead. In these the color of the fluorescence and phosphorescence is often different. This, they say, is due to the fluorescence being caused by the decomposition of the salt with the formation of the subchloride, bromide or iodide, while the phosphorescence is due to the change back into the original compound or to the decomposition of the sub-salt. Further, the residue after the action of the cathode rays is always colored, varying from blue to brown or black, depending both upon the nature of the salt and the duration of the cathode discharge.

Under the second group are placed the sulphates of the alkalies, salts of the alkaline earth and magnesium groups and some of the heavier metals. These differ from the first group only in showing no colored residue after the action of

[1] Curie: Ibid., **129**, 823 (1899).

[2] Wiedemann and Schmidt: Wied. Ann., **54**, 622 (1895); **56**, 203 (1895); **64**, 78 (1898).

the cathode rays. However, some of these, after long exposure, do show a slight decomposition and so the distinction between the first and second group is one of degree only.

Wiedemann and Schmidt say that under the cathode rays the color of the phosphorescence of the salts of any metal is independent of the nature of the acid radical. All salts of the same metal give the same color, differing only in intensity. This is illustrated with cadmium and uranium salts, the former giving yellow phosphorescence and the latter green.

Under the third group they place all the rest of the simple salts which they tried and found no light effect.

Goldstein[1] tried the effect of the cathode rays upon a number of the alkaline halides and found that they changed color but regained the original color on being heated or by the action of moist air. He ascribed the change to a physical modification and not to any chemical action taking place.

If, as Wiedemann and Schmidt suggest, the phosphorescence under cathode rays is due to the recombining of the parts of the compound which have been separated by the action of the cathode rays; then, if these parts are brought together and their combination brought about in the ordinary way, light of the same color as the phosphorescence or fluorescence should be emitted. It was for the purpose of duplicating the color of the light given out by the phosphorescence and fluorescence of these bodies that this work was undertaken.

Schluederberg[2] has shown that when an alternating current is passed through a dilute solution of sulphuric acid, using lead electrodes, a luminescence can be seen around the electrodes, becoming brighter as the solution fills up with the insoluble lead sulphate. This light must be due to the formation of lead sulphate, since with platinum or unattackable electrodes no light can be detected.

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[1] Goldstein: Wied. Ann., **54**, 371 (1894).

[2] Schluederberg: Jour. Phys. Chem., **12**, 623 (1908).

This experiment was repeated and tried with other metals and solutions. The solutions used were saturated potassium bromide and iodide, dilute and concentrated sulphuric acid and dilute hydrochloric acid. The metals that were tried were cadmium, zinc, lead, copper, silver, mercury and magnesium.

The electrodes were wires or thin strips of the metals about the size of a No. 16 wire, B. and S. gauge. Those were immersed in the electrolyte from two to four centimeters. In every solution the experiment was first run with platinum electrodes to see if the light was due to a state of static discharge. In no case was there any light observed with platinum electrodes. However, with the concentrated sulphuric acid the color of the light emitted was nearly always the same and from the fact that with a current of 6 amperes the voltage across the cell was from 50 to 70 volts it is probable that here the light is due to a static discharge. This is the more probable from the fact that those metals which tend to become passive give the brightest light in the concentrated sulphuric acid, for example magnesium. With the dilute acids and the salt solutions the voltage never was high, being from 6 to 8 volts with 6 amperes flowing.

In all cases where the light was intense enough, it was examined with a spectroscope and found to give a continuous spectrum which would be brighter in one part. This is true of the spectra of the phosphorescence of most inorganic salts, the spectrum will be continuous but brighter in one or more parts.

In cases where the light is very faint it can be observed only after remaining in the dark for fifteen or twenty minutes so that one's eyes become sensitive.

Schluederberg used an alternating current with the lead in sulphuric acid but with all the other metals better results were obtained with the direct current, the light effect then appearing only around the anode.

The results are given in Table I:

TABLE I

	Cd	Zn	Pb	Cu	Ag	Hg	Mg
KBr	—	—	Faint bluish white	Faint white	Very faint violet white	Brilliant orange	—
KI	Intense yellow white	—	Brilliant yellow	Faint red (?)	Very faint	Orange	—
H_2SO_4 1:4	Yellow white bright	White	White greenish (?)	—	White very bright	Yellow	—
H_2SO_4 conc.	Very brilliant yellow white	Very bright greenish white	Very bright greenish white	Greenish white	—	Greenish white (weak)	Greenish white very bright
HCl	—	—	Faint	Green very (weak)	Yellow faint	Yellow orange bright	—

As is shown in Table I the cases where there is no light are where the salts formed are soluble, this would seem to show that one thing necessary is that the metal in corroding must form the solid salt and not remain in the dissolved state.

During electrolysis in a solution of potassium bromide cadmium electrodes give a precipitate of cadmium hydroxide, the bromide formed being soluble. In hydrochlor c acid no precipitate is formed and in neither of these cases is any light given out. In potassium iodide solution a film forms on the electrode and light is given out; the same thing is true with sulphuric acid.

Zinc electrodes in the bromide and iodide solutions give a white precipitate of the zinc hydroxides, but no light is produced since the zinc salts are soluble. In hydrochloric acid no precipitate is formed and there is no light produced. In concentrated sulphuric acid there is a precipitate formed and a light effect shown.

Lead gives a precipitate in every case and gives more or less light in every case.

Copper in hydrochloric acid gives but a very thin film of cuprous chloride on the electrode and the light effect is very weak. With a copper electrode in potassium bromide the current at first seems to set free bromine and this could be seen flowing from the electrode, but this soon ceased and a yellow precipitate was formed which was dissolved by adding a few drops of hydrochloric acid to the solution. As shown in the table the light effect was weak. In potassium iodide solution the copper becomes covered with a thin film of cuprous iodide while the solution turns dark, due to iodine set free. The light effect was weak. In dilute sulphuric acid there is no precipitate and no light produced. In concentrated sulphuric acid the precipitate formed is finally divided copper and not copper sulphate.

Silver gives a precipitate in every case and also gives light in every case; and the same is true of mercury.

With mercury in a solution of potassium iodide the pre-

cipitate is yellowish white with a circle of red next to the mercury. In potassium bromide and sulphuric acid the precipitate is greenish white. In hydrochloric acid the precipitate is a grayish black slime.

Magnesium gives no precipitate in any of the solutions and gives no light in any except the concentrated sulphuric acid.

When the salt formed is very insoluble, in order to observe the light effect it is necessary to watch carefully just at the moment the circuit is closed either by closing the switch or by holding the electrode in the hand and dipping it into the solution, after the eyes are fully accustomed to the darkness.

A special case of this is that of cadmium in potassium iodide solution. When the circuit is first closed there is no light effect for about a second, then a bright yellow luminescence is seen to travel from the bottom to the top of the anode and after that there is no more light to be noticed. This same thing is repeated each time the circuit is closed or the electrode dipped into the solution. If the process is observed in the light, on first closing the switch the electrode turns brown, growing darker and darker until the flash comes and after that it is white, being covered with a film of the iodide. This remains until the circuit is opened and it dissolves off. It is probable that light is being given off beneath the white film but it cannot be seen. There is always about a second between the closing of the circuit and the appearance of the flash.

With cadmium electrodes no luminescence was obtained in potassium bromide or hydrochloric acid. With the iodide as noted above a bright yellow or yellow white was seen for an instant. Dilute sulphuric acid gives a similar bright flash. With concentrated sulphuric acid there is obtained around the anode a very bright light which gives a continuous spectrum with the direct vision spectroscope but appears yellow to the naked eye.

Zinc electrodes give positive results only with sulphuric

acid. In dilute acid there was but little effect but as the concentration of the acid was increased the light became stronger and with concentrated acid the anode was surrounded by a bright greenish white luminescence. The solution became very hot and was filled with a white precipitate.

With lead in potassium bromide the light was bluish white but not very bright, a dense yellowish white precipitate being formed. With potassium iodide a bright yellow luminescence was obtained but it would not last very long because of the film of lead iodide clinging to the electrodes and cutting off the light. Wherever this film would break the light could be seen as a little spark. With hydrochloric acid the light effect was not very bright but was quite noticeable after the current had been running for some time, especially at the lower end of the electrode. As Schluederberg has shown, with dilute sulphuric acid and a direct current no light effect was observed because the anode became covered with a film of lead peroxide and no more lead would dissolve. With an alternating current and a 1 : 10 sulphuric acid solution a faint luminescence was obtained; this increased in brightness with the concentration of the acid. With very concentrated acid it becomes quite bright, being white in color. It gives a continuous spectrum with the direct vision spectroscope.

Copper electrodes in potassium iodide gave no definite light effect although with a very high current density the anode seemed to give out a very faint reddish light. With potassium bromide the light was a faint white with a tendency toward violet. The solution turns brown and a precipitate is formed. In rather concentrated hydrochloric acid only a few flashes of light were obtained and these were too faint for the color to be distinguished With dilute sulphuric acid there was no light effect but in the concentrated acid there was a flash of green just at the moment the circuit was closed. The solution fills up with fine particles of copper due to the solution of the copper as the "ous" salt and its decomposing in the solution.

Of all the metals that were tried the best results were obtained with mercury electrodes. The mercury was held in a glass tube bent in the form of a hook, with the end broadened out like a funnel or thistle tube. Connection was made by dipping copper wires into the long arm of the tube. This gives a mercury surface of about a square centimeter for the electrode. When immersed in a solution of potassium iodide, 300 grams to the liter, and the circuit closed, a very bright orange or reddish yellow light is obtained, which lasts quite a few seconds. Besides this light there is always a circle of violet where the mercury and glass meet. This last is always neglected. With potassium bromide an orange colored light is seen, best just after the circuit is closed. With dilute sulphuric acid a bright yellow is produced. The mercurous sulphate formed cuts off the light very quickly but, by shaking this off the surface, the light will appear again. Better results were obtained by cutting the current down from 6 to 3 amperes and using a 1 : 3 solution of sulphuric acid instead of a 1 : 10 as with the other metals. With the concentrated sulphuric acid there is less light effect and it is more greenish white in color. The film of sulphate is formed immediately. With dilute hydrochloric acid, 1 : 10, the mercury gives a yellowish orange light but becomes covered with a mass of black slime which cuts off the light very quickly.

Silver electrodes in potassium iodide and potassium bromide solutions give a few flashes of light but the film of the silver salt forms so quickly that it is impossible to distinguish the color. The bromide gives a light, slightly blue or violet in color. An alternating current gives no better results. Dilute sulphuric acid gives a bright white light. In hydrochloric acid the silver chloride sticks very tight and cuts off the light very quickly but if the current is allowed to flow for some time little patches of yellow light can be seen running down the anode.

Magnesium gives nothing with any solution except the concentrated sulphuric acid and, as mentioned before, this is probably due to a static discharge. When the current was

reversed, the magnesium being made cathode and platinum anode, there was no light effect.

From these results it is seen that when these compounds, the chlorides, bromides, iodides and sulphates are formed, light is given off and on comparing the color of the light with that of the fluorescence and phosphorescence under the cathode rays as given in Table III later in the article it can be seen that in most cases there is a good agreement between them. This is especially true of the mercury salts.

Experiments on Direct Chemical Combination

The next experiments were to duplicate these light effects by chemical combination without the use of the electric current. Each metal was placed in a porcelain boat in a hard glass combustion tube and after being heated above the melting point, where this was possible, a current of chlorine, bromine or iodine vapor was passed over it and the light effect observed. The chlorine was obtained from a cylinder and was passed through water in a gas wash bottle to enable one to regulate the current and also because the alkalies do not react with dry chlorine very readily.[1] The bromine and iodine vapors were obtained by placing the liquid or solid in a 100 cc flask with a delivery tube running to the combustion tubing in which the metals were heated. When the metals were at the desired temperature the flask was immersed in hot water and the stopcock between it and the combustion tubing opened, while suction was applied to the other end thus drawing the vapors over into the tube.

On account of its striking fluorescent color under the cathode rays cuprous iodide was the first one tried. When heated in the combustion tube and iodine vapor allowed to act on it the reaction was apparently not vigorous enough to give off light.

McLean[2] showed that when copper foil is heated in the air and iodoform sprinkled on it, dense fumes of iodine are

[1] Merz and Holzmann: Ber. chem. Ges., Berlin, **22**, 837 (1889); Cowper: Jour. Chem. Soc., **43**, 155 (1883).

[2] Jour. Chem. Soc., **73**, 153 (1898).

TABLE II

	Chlorine	Bromine	Iodine	Oxygen or sodium peroxide	Persulphate
Cu	Melts with a cherry red Glows only	—	Purple red	—	—
Hg	Greenish yellow	Yellow orange	Orange to red brown	—	—
Ag	—	White faint	—	—	—
Cd	Bright greenish yellow	—	—	Yellow	White and blue white
Pb	White very faint	Weak white	—	—	Blue
Na	Blue	Blue white	White greenish (?)	Blue	Blue
K	Deep blue	Blue	White green	—	Blue
Zn	—	—	—	White varying from bluish to greenish	Green white varying to blue white
As	—	—	—	White varying from green to violet	—

given off and a bright red flame passes over the foil. This was repeated but the flame is probably due to the oxidation of the carbon in the iodoform and not to the formation of cuprous iodide. The same experiment was tried with copper and iodine and with hydriodic acid but without obtaining any light effect. If powdered copper is used instead of copper foil it oxidizes too quickly in the air on heating. After trying many ways of bringing iodine and copper together it was found that when the copper is heated gently and a few crystals of iodine added to it, the two unite and a reddish violet light is produced, while the white cuprous iodide remains after the action.

Copper heated in a current of moist chlorine glows with a cherry red glow, but otherwise there is no light effect.

Mercury heated to boiling in a current of chlorine burns with a greenish yellow flame forming the mercuric chloride. With bromine it gives a very bright yellow orange and with iodine an orange which appears at times reddish brown as seen through the iodine vapor.

Silver gave nothing with either chlorine or iodine, but with bromine it gave a faint white. The chloride forms a film and prevents further action.

Lead gives a faint white with chlorine and bromine but nothing with iodine. With the chlorine there was always a flash of white just as the chlorine was run in and started to unite with the molten lead.

Cadmium gave a bright yellow bordering on the green with chlorine. The metal remains molten, as does the chloride formed, and floats around on top of the fused salt. The latter is somewhat red in color and the yellow color of the light due to the combination of the metal with the gas is seen above this. Cadmium gives nothing with either bromine or iodine.

When trying some experiments upon the decomposition of mercuric chloride with metallic sodium which will be described later, a bluish white luminescence was obtained; but

on tracing this down it was found to be due to the slow oxidation of the metallic sodium.

Wiedemann and Schmidt[1] showed that the thermoluminescence or phosphorescence of sodium chloride was blue and if this is due, as we think, to the recombination of the chlorine and sodium which have been set free by the cathode rays then the combination of these should give a blue light. As was seen with sodium and the oxygen in the air the slow union did give that color and therefore the same thing was to be expected with chlorine.

When a slow current of chlorine is passed over metallic sodium, in the form of a fine wire, placed in the combustion tubing at ordinary temperatures the sodium gives quite a bright light-blue luminescence and the brightness increases with the strength of the chlorine current until the sodium bursts into flame with the usual color. If allowed to react slowly the metal becomes covered with a layer of the chloride and the luminescence will cease.

To show that the blue light was not due to the oxygen of the air the tube was first swept out with dry hydrogen and then chlorine was run in. As soon as the chlorine came in contact with the metal the light was seen. The current of chlorine was increased until the sodium burst into flame and this set off the mixture of hydrogen and chlorine and a slight explosion resulted. This shows that the blue light can be caused by chlorine as well as by oxygen. The same thing was tried with bromine and iodine; the former gives a bluish white light, weaker than with chlorine, while the latter gives a white light with a trace of green.

Potassium treated in the same way reacts much more violently with chlorine than sodium does and therefore it is harder to get the slow combustion to show as well. However, at the end of the piece of potassium towards the cylinder there was always a deep blue light, very different from the characteristic violet of potassium. The heat of the reaction is so great that in nearly every experiment the glass tubing

[1] Wied. Ann., 56, 203 (1895).

was broken. The residue left behind after the action was always colored greenish blue, but if allowed to stand in the open air for twenty-four hours it would lose all the blue color and become yellowish white. This blue is caused by the excess of potassium remaining unacted upon; by the action of the moisture in the air this is converted over into the hydroxide and thus destroys the color. With bromine, potassium gave a bluish green light, which was stronger than bromine with sodium but weaker than the potassium with chlorine. With iodine the potassium gave a faint white, colored slightly green. This could best be seen by placing some crystals of iodine upon a piece of potassium in a porcelain boat and warming gently.

Light Due to Formation of Oxides

This was brought out in two ways, either by burning the metal in a stream of oxygen or by adding sodium peroxide to the molten metal.

Bismuth, tin, zinc and cadmium all give negative results when heated in a current of oxygen. However, when cadmium is heated with a blast lamp until it volatilizes, it combines with oxygen and burns with a deep yellow flame to the reddish brown oxide. Zinc heated in the blast to boiling burns with a green flame.

Arsenic gives peculiar results in that the color of the flame depends entirely upon the rate at which the oxygen is run into the tube. When pure oxygen is used, the color of the flame is a bluish white with now and then a flash of green for a moment. When air is used the color tends more towards the yellow green. If the air or oxygen supply is cut down very low so that the arsenic just barely burns, the color of the flame is green, and by increasing the supply one can vary the color from a green up to the blue.

When sodium is oxidized with a very slow current of oxygen the luminescence is blue and the sodium is converted into a white powder, but when the oxidation is done rapidly the sodium burns with the characteristic yellow flame and leaves a yellowish white residue of the peroxide.

If a piece of sodium is placed on water, a trail of bluish white light follows it; as it rolls around over the surface the color is similar to that when sodium is oxidized slowly. Apparently then in all these cases where sodium reacts slowly the color of the luminescence is blue; at least this has been shown in the case of its action on chlorine, bromine, iodine, oxygen and water.

Experiments with Sodium Peroxide

Molten lead treated with sodium peroxide reacts very violently, the heat of the reaction being sufficient to fuse the whole mass, which becomes cherry-red, but otherwise there is no luminescence visible.

Cadmium in the same way is changed to the brown oxide and the mass during the reaction resembles burning soot.

Copper powder oxidizes too easily in the air on heating to show any luminescence.

When molten zinc is treated with a large amount of sodium peroxide it reacts violently, blows out of the crucible, and nearly every time breaks the bottom out of the crucible. When the peroxide was added a little at a time to the molten metal, there was a popping and splattering; but the flame was visible and varied from a blue to a green with a tendency towards the green.

Experiments with Ammonium Persulphate

On the basis that the fluorescence and phosphorescence of the sulphates is due to the recombination of the metal with the SO_4 radical after being separated by the cathode rays, an attempt was made to duplicate this by the action of the molten metal upon ammonium persulphate, which will break down into ammonium sulphate and the sulphate group SO_4. The latter, on being set free, will react with the metal.

Molten lead treated with the persulphate gives a bluish white light just as the mass is solidifying. This can best be seen by stirring the mass with a glass rod and as it solidifies a bluish white streak of light will follow the rod.

Cadmium in the same way gives a white streak and zinc gives a greenish white.

After the violence of the reaction on first adding the persulphate, sodium and potassium give a blue or blue-green luminescence. Mercury gives no light effect. When calcium is heated to a bright red heat before adding the persulphate, it gives a flash of white just at the moment the persulphate is added and before a film of the calcium sulphate is formed. The light ceases almost immediately.

Since the ammonium persulphate breaks down so readily and gives off dense fumes which obscure the light effect, the potassium salt was tried instead. This deepens the blue of the lead when added to the white hot metal, gives a greenish blue with cadmium and a blue with zinc.

Apparently there is a new factor that has entered into the question and that is the light due to the decomposition of the potassium persulphate or, viewed from the other side, the formation of the potassium sulphate from the persulphate. As was seen, the action of ammonium persulphate on metallic potassium gave a blue luminescence, so the formation of potassium sulphate is accompanied by a blue light effect. Potassium persulphate was added to hot powdered charcoal and the same blue was obtained although weaker than when the metals were present. This shows that the decomposition of the persulphate or the formation of the sulphate gives a blue light.

Next, some persulphuric acid was prepared by treating a saturated solution of the ammonium salt with concentrated sulphuric acid while the solution was kept cold in a freezing mixture. Some of the clear solution was pipetted off and added to molten lead, cadmium and zinc when results similar to those with ammonium persulphate were obtained. Next, concentrated sulphuric acid was added to the molten metals and all gave a faint blue.

The peculiar point about the light is that it does not come from all over the surface of the hot metal but from along the sides of the crucible and where there are holes in the sur-

face of the persulphate crust. Apparently the light comes from below and is reflected upon the vapors of the decomposing sulphate.

These experiments seem to show that the sulphates have their own color of luminescence due to their formation, but that this is often masked by the light due to the decomposition of the persulphate.

Experiments with Solid Sulphur Trioxide

As it is possible that the cathode rays might cause a sulphate to decompose into the oxide and sulphur trioxide, instead of into the metal and the sulphate group, and since the light would then be due to the recombining of these, some experiments were made on the action of solid sulphur trioxide on heated metallic oxides.

Cadmium oxide gives a bright yellow light, zinc oxide a bright green, lead oxide a white, while calcium, barium and strontium oxides all give a bright yellowish white light which is not characteristic.

Experiments with Hydrofluoric Acid

When metallic sodium is added to hydrofluoric acid in a platinum dish, it floats around over the top just as it does on water. By close observation a faint bluish white light could be seen following the metal globule. The light was probably due to the water in the acid as the light was of the same color, but less intense then when sodium acts upon water.

Potassium reacts much more violently, the globule of metal exploding almost as soon as it strikes the liquid. Calcium and magnesium gave no light effect.

These experiments with hydrofluoric acid are hardly to be considered as similar to the preceding ones or to those that take place during fluorescence and phosphorescence under the cathode rays, because they are metathetical reactions and not a direct union of the elements.

Another similar experiment which is open to the same objection was tried. A saturated solution of lead acetate

was added to a saturated solution of sodium sulphate in the dark, both solutions having first been heated to boiling. No light effect was observed during the formation of the precipitate of lead sulphate. The same thing was tried with lead acetate and concentrated sulphuric acid but with negative results; also with mercurous nitrate and potassium chloride.

A saturated solution of cadmium sulphate was treated with concentrated sulphuric acid to see if there would be any light given out during the crystallization of cadmium sulphate from the solution. This also gave negative results.

These experiments show that, at least in water solutions, these metathetical reactions will not produce any luminescence.

Experiments on the Decomposition of Phosphorescent Salts

Up to this time the experiments have been dealing with the light given out by the combining of the elements or the metal with the acid radical, and it has been shown that in many cases there is a coincidence between the color of the light given by the chemical action and that of the fluorescence or phosphorescence under the cathode rays. The question may be asked whether the light might not be due also to the decomposition of the compounds also. An attempt was made to decompose the phosphorescent salts with metallic sodium both by heating them and by grinding them together in a mortar.

Lead sulphate, lead oxide, zinc oxide, mercurous and mercuric chlorides and cuprous iodide were treated in this way but no light effect was noticed except the bluish white due to the slow oxidation of the sodium in the air or possibly the combination of the sodium with the chlorine, iodine or sulphate group. The mercurous and mercuric chlorides turned black and yellow respectively showing that decomposition had taken place but in no case was any light observed except that due to the sodium.

The same result was obtained by adding molten sodium

to hot mercuric chloride, no light except that due to the sodium being observed.

Electrolysis of Fused Salts

P. Lenard[1] has shown that the molten salts of the alkali metals have a glow which varies with the metals and is independent of the acid radical present.

Lithium glows with a blue color, sodium blue, potassium green and rubidium and caesium with a yellow green.

As will be seen these colors agree with the phosphorescent colors of the alkali metals and it was thought that this light might be due to the formation of different salts by a reaction between the parts similar to what takes place in phosphorescence.

By electrolyzing the molten salt with an alternating current it was thought that possibly the two being set free at the same electrode might unite and give out this light. Although several of the salts were tried only negative results were obtained.

Lenard accounts for the color as due to the free metal atom and says each metal has its own particular color.

Theoretical

There are four possible explanations for the phenomena of phosphorescence and fluorescence under cathode rays as due to chemical action.[2]

I. The decomposition of the compound gives out light.

II. The recombination of the dissociated parts gives out light.

III. Both decomposition and recombination give out light.

IV. The change to allotropic forms gives out light.

If the first of these is the explanation, and the light is due to decomposition brought about by the exciting agents, either cathode rays, sunlight, spark discharge or anything

[1] Drude's Ann., 17, 199 (1905).

[2] Wiedemann and Schmidt: Wied. Ann., 56, 243 (1895).

else, it will be visible only during the time of excitation. Therefore there can be no phosphorescence or thermophosphorescence.

If the second is the explanation there can be all three and the light given out will always be the same color. As soon as the excitation starts, some of the compound will be decomposed and the parts will tend to reunite and give out light. Finally, a state of equilibrium will be reached between the decomposition and recombination. When the excitation is stopped the recombination will continue and give phosphorescence. If the temperature is raised, the velocity of the reaction of recombination will be increased and we shall have thermoluminescence, the fluorescent, phosphorescent and thermophosphorescent lights, all being of the same color because they are all due to the same reaction.

If, as in the third class, both the decomposition and recombination produce light, these may be of the same color or they may be of entirely different colors. If of the same color, then the fluorescence, phosphorescence and thermophosphorescence will have the same color and it would be hard or impossible to distinguish between this case and that where recombination alone gave the light. However, if the decomposition gives a different light from the recombination then there will be a difference between the color of the fluorescence and the phosphorescence. The fluorescence is the color of the decomposition modified by the recombination that takes place during the excitation. The phosphorescence will have the color due to recombining alone. At all times the thermoluminescence will be the same as the phosphorescence since it is due merely to an increased velocity of the recombination.

In all cases of phosphorescence the duration of the light will depend upon the velocity of the recombination and it is possible that this velocity may be so great that there will be no phosphorescence even if the light is due to a recombination.

There is always a possibility that instead of it being the decomposition or the reformation of the original body that gives the light, the fluorescence and phosphorescence may be due to the formation or decomposition or a third body which is formed by the exciting agent. To simplify this it can be put in the form of symbols, where A stands for the original substance, B the decomposition products under the cathode rays, C is the second decomposition product formed by the action of the cathode rays upon B.

I. $A \longrightarrow B$ gives out light.

II. $A \longleftarrow B$ gives out light.

III. $A \rightleftarrows B$ both give out light.

IV. $A \rightleftarrows B \longrightarrow C$; change from B to C gives out light.

V. $A \rightleftarrows B$; change from C to A gives out light.

$$\begin{array}{ccc} A & \rightleftarrows & B \\ & \nwarrow\ \swarrow & \\ & C & \end{array}$$

If the light is due to allotropic changes the above reasoning will hold just as for chemical action. An equilibrium will be reached between $A \rightleftarrows B \rightleftarrows C$ and the fluorescence and phosphorescence will depend upon which one of the transformations gives out light.

Consider these groups separately. There is no example which can definitely be placed under the first group. The case of aluminum oxide studied by Wien[1] which will be discussed later would seem to come under this group, but after examination it is found that it does not.

Under the second group, where it is simple combination that causes the light, can be placed those cases where both phosphorescence and fluorescence are of the same color and the same as the thermoluminescence. However, as mentioned before, it is not necessary that there shall be all three as the velocity of combination may be so great that the last two will be unnoticeable. In this group can be placed the larger part of the phosphorescent inorganic bodies as can be seen in Table III which is given later.

[1] Wien: Phys. Zeit., 3, 440 (1902).

In the third class or group where both decomposition and recombination give out light we can place definitely those salts which have a different fluorescent color from a phosphorescent. Besides these probably there are some of the cases where the light is the same color that fall into this group but they cannot be distinguished at present. The chief members of this group are the alkaline halides. As can be seen in Table III in nearly all cases the fluorescence is different from the phosphorescence. By a comparison of the colors with those given off by the direct combination shown in the beginning of the paper it is seen that it is the phosphorescent light that agrees, therefore it agrees with our theory that the phosphorescent light is due to the recombination. Take the case of sodium chloride for example.

Fluorescence under cathode rays whitish, slightly blue.
Phosphorescence weak.
Thermophosphorescence bright blue.

Under the fourth group where the light is due to the reaction between a second decomposition product of the cathode rays, there is one example known, that of sodium peroxide. The cathode rays decompose the peroxide into the oxide and oxygen, and this reaction is not accompanied by light. Then the cathode rays decompose this oxide into sodium and oxygen and the recombination of Na and oxygen give the light.

At present there are no examples of the fifth group known, but probably when the problem of phosphorescence is studied along this line some examples will be found.

In Group VI may be placed calcium sulphide whose phosphorescence has been shown to be due to allotropic transformations.[1]

Phosphorescence of Aluminum Oxide

Wien[2] has shown that aluminum oxide prepared by precipitation and dehydration of the hydroxide is not fluor-

[1] Waentig: Zeit. phys. Chem., **51**, 471 (1905).
[2] Wien: Phys. Zeit., **3**, 440 (1902).

escent or phosphorescent under the cathode rays, while that which is prepared by burning the aluminum powder in the air or in oxygen is fluorescent and phosphorescent under the cathode rays and gives off oxygen during the action of the cathode rays. This might seem to be an example of the first group where the light is due to the decomposition of the substance, but since it shows phosphorescence after the exciting agent has ceased, the light cannot be due entirely to the decomposition.

Since the ordinary aluminum oxide does not show this fluorescence, while that formed by burning the metal in air does, there must be some difference between the two and this can be due either to the metal burning to some other compound, say a peroxide, or to the metal having impurities present in it which cause the fluorescence after burning in air.

Some aluminum peroxide was prepared by the method of Gibson and Morrison[1] by precipitating the peroxide with an alkali and adding an excess of the latter to just dissolve the precipitate, then adding hydrogen peroxide, filtering off the precipitate formed and drying at 110° C. This material showed no light effect under the cathode rays, and so the peroxide theory is eliminated.

Owing to the method of preparation of metallic aluminum by the electrolysis of bauxite in a fused bath of cryolite the natural impurity present would be sodium. If this were present it would burn in the air to sodium peroxide and this under the action of the cathode rays might give off oxygen due to its decomposition.

Some sodium peroxide was exposed to the action of the cathode rays for an hour. At first there was no light effect, but by keeping the pump going all the time and thus keeping a high vacuum the oxide became fluorescent and showed phosphorescence of very short duration. The color of the light was a yellowish white, the same as that shown by the aluminum oxide. The only difference was in the duration of the phosphorescence, that from the sodium peroxide last-

[1] Proc. Roy. Soc., Edin., **119**, 146.

ing but a fraction of a second while the aluminum oxide remained bright for several minutes. The sodium peroxide gradually turned white on the surface, due probably to the formation of sodium oxide and the liberation of oxygen. After an exposure of more than an hour the surface had turned slightly brown, due to metallic sodium from the decomposition of the oxide.

Sodium peroxide was added to aluminum oxide which had been prepared by the usual precipitation method and showed no fluorescence under the cathode rays. These were ground together and then heated until the mass just caked. On exposure to the cathode rays after cooling, the fluorescence and phosphorescence was of the same color and intensity as that of the aluminum oxide prepared by burning in air, the only difference being the duration of the phosphorescence.

The surface of the material was a deep blue color after an exposure of half an hour to the cathode rays. On the addition of water to this blue it turned white and gave off bubbles of gas. This blue is probably the metallic sodium dissolved in the mixture of the two oxides.

On the supposition that the sodium peroxide united with the aluminum oxide to form sodium aluminate, some sodium aluminate was prepared by dissolving the aluminum hydroxide in an excess of sodium hydroxide and evaporating to dryness. This showed fluorescence but the residue was not colored blue by the cathode rays even after an exposure of over an hour. This material differed from the mixture of the two oxides that did turn blue, by having an excess of alkali instead of an excess of alumina, so some sodium hydroxide was added to an excess of aluminum hydroxide and the mixture evaporated to dryness and ignited over a blast lamp. This on exposure to the cathode rays gave a deep blue residue and showed the same fluorescence as before. Besides this there were some spots where the mixture had a blue fluorescence.

The excess of alkali in the first aluminate prevented

the formation of the blue either because the water was not all out of the mixture, being retained by the alkali; or because it prevented the sodium from dissolving in the aluminate when it was set free by the cathode rays.

These results seem to show that the fluorescence and phosphorescence of aluminum oxide, prepared by burning the metal in air, is due to the presence of sodium in the aluminum; when the alloy burns the sodium is converted into the peroxide.

Pure alumina shows no fluorescence or phosphorescence under the cathode rays. Sodium peroxide shows fluorescence and phosphorescence under the cathode rays in a high vacuum after a long exposure. This is due to the reaction between the sodium and oxygen which are the products of the second stage in the decomposition of the sodium peroxide, which takes place in the following steps:

$$Na_2O_2 = Na_2O + O = 2Na + O_2.$$

There is apparently no light given out by the decomposition of the peroxide in the first stage but the light is due either to the decomposition of the Na_2O or to its reformation after being decomposed by the cathode rays. The residue after the action of the cathode rays was brown, due to the metallic sodium set free.

Sodium aluminate showed fluorescence and phosphorescence under the cathode rays, the same color as that of aluminum oxide prepared by burning the metal in air. Beside this yellow white light it also showed spots of blue fluorescence.

The residue after the action of the cathode rays was colored a deep blue, due to a solution of the sodium in the aluminate. The same results were obtained by mixing the sodium peroxide with an excess of aluminum oxide. However, when the aluminate is prepared with an excess of alkali present, this prevents the sodium from being set free and dissolving in the aluminate and hence the residue does not turn blue.

We may consider then the sodium present in the aluminum oxide prepared by burning the metal in air to be there in the

form of peroxide. This will account for the liberation of oxygen and the fluorescence and phosphorescence.

If the sodium peroxide unites with the aluminum to form the aluminate and is present in that form the light given out would be due to the decomposition or reformation of the aluminate.

Whether it is there as the peroxide or the aluminate could no doubt be decided by the rate at which oxygen is liberated by the action of the cathode rays since it would be more rapid in the decomposition of the peroxide than the aluminate. No experiments were made to ascertain this point.

Phosphorescence of Alkaline Halides

Wiedemann and Schmidt account for the color changes that take place in the halides of the alkali metals by assuming the formation of a sub-salt of the formula X_2Cl, or of the setting free of the free metal. They assume the formation of the sub-salt for the following reasons:

(1) The substance formed by the action of the cathode rays reacts alkaline to litmus or phenolphthaleine.

(2) The halogen is given off during the exposure.

(3) Sub-salts prepared by the electrolysis of the molten salt have the same properties as the substance formed by action of the cathode rays. They react alkaline, have the same color, show thermo- and lyo-luminescence, lose their color and become white on heating or by action of moist air.

They account for the alkalinity of the sub-salt by this reaction:

$$Na_2Cl + H_2O = NaOH + NaCl + H.$$

Kirchhoff and Bunsen[1] and Rose[2] were the first to describe these sub-salts of the alkalies. R. Lorenz in his "Elektrolyse geschmolzener Salze" has shown that during the electrolysis of fused salts there is formed what he terms a "metal fog," of the particles of metal suspended in the molten salt. It is really a colloidal suspension of the metal in the melt.

[1] Pogg. Ann., 113, 345 (1861).
[2] Ibid., 120, 1 (1863).

Zsigmondy in "Zur Erkenntnis der Kolloide," page 58, has shown that when the blue form of sodium chloride is examined with the ultramicroscope fine particles of the metal can be seen.

From this it is apparent that instead of the color of the substances formed by action of the cathode rays or by electrolysis of the fused salt being due to a sub-salt, they are probably due to the finely divided metal. As mentioned before, when a piece of sodium is dropped on water it gives off a faint or pale blue light as it floats over the surface, due to its action on the water. This will account for the luminescence or phosphorescence when the so-called sub-salt goes into solution.

When metallic sodium is rubbed in a mortar it reacts with oxygen and gives a pale blue light. This will account for the frictional phosphorescence of the sub-salt.

Since the method of preparing the sub-salts by electrolyzing the fused salts was ideal for obtaining this metal fog through the mass, it is to be expected that they would show the reactions for the metals.

In the case of the halogen salts, there is practically no question as to what the reacting bodies are that give the light. It is either the reaction of the halogen upon the metal or possibly upon the subchloride. In the case of the alkalies the former reactions have been shown to be the more probable. However, when we consider the case of the sulphates the question is not so simple, as the reaction may be between:

(1) Metal and SO_4.

(2) Metal and oxygen.

(3) Oxide and sulphur trioxide.

Take the three sulphates that were studied, cadmium, lead and zinc, and consider the data to see which of these explain the phenomena.

Cadmium Sulphate.

$Cd + O$ = gives a bright yellow light.

$CdO + SO_3$ = gives a bright yellow.

$Cd + (NH_4)_2S_2O_8$ gives white (weak).

Cd + H_2SO_4 in electrolysis yellowish white.

CdO + $(NH_4)_2S_2O_8$ = nothing.

Fluorescence and phosphorescence in cathode rays gives a bright yellow.

It would seem in this case that the light must be due either to the formation of the oxide or to the action between the oxide and sulphur trioxide. When sulphuric acid is electrolyzed between cadmium electrodes the anode first becomes covered with a brown film of the oxide and the formation of this does not give out light. This turns white and in doing so a flash of light is seen. One would therefore say that the light does not come from the formation of the oxide. Hence it must come from the action of sulphur trioxide upon the oxide. That this is the reaction is also shown by the fact that when cadmium sulphate is exposed to strong and prolonged cathode rays it becomes covered on the surface with a yellow powder which resembles the oxide.

Zinc Sulphate.

Zinc + O = gives a bright green.

Zn + Na_2O_2 = bright greenish white.

Zn + $(NH_4)_2S_2O_8$ = bluish white.

Zn + H_2SO_4 in electrolysis gives greenish white.

ZnO + SO_3 = very bright green.

Zinc sulphate in cathode rays fluoresces bluish white or Wiedemann and Schmidt call it white.

From the above it can be seen that the phosphorescence of zinc sulphate cannot be due to the action of SO_3 on the oxide and must be due to the action of SO_4 on the metal.

Lead Sulphate.

Pb + O = gave no light effect.

Pb + Na_2O_2 = gave nothing definite.

PbO + SO_3 = white.

Pb + $(NH_4)_2S_2O_8$ = blue.

Pb + H_2SO_4 by electrolysis apparently white but too faint to judge well.

PbO has a white fluorescence in cathode rays.

$PbSO_4$ has a bright blue fluorescence in cathode rays.

Here, as in the case of zinc sulphate, the fluorescence cannot be due to the action of the sulphur trioxide upon the oxide as this gives white.

Since the formation of the lead sulphate by the action of the persulphates gives a blue light this must be the reaction that takes place during the fluorescence, namely the union of the lead and the SO_4 ion.

Further, the action of a heavy and continued discharge of cathode rays upon lead sulphate leaves the surface covered with a black or grayish black powder which is insoluble in sodium acetate and hence cannot be the oxide and must be the finely divided metal.

On repeating the observations of Wiedemann and Schmidt on the phosphorescence of the inorganic salts in the cathode rays there was a good agreement with their results in nearly all cases but in a few instances the compounds failed to show any fluorescence, zinc oxide and sulphate and lead oxide being the chief ones. The cadmium sulphate that was first tried was a sample from DeHaën and showed a very brilliant fluorescence and phosphorescence. A sample from Baker and Adamson was much fainter and one from Kahlbaum which was marked 99.99 percent pure did not show any light at all.

On microchemical analysis the material from DeHaën showed quite a strong test for sodium, a less one for zinc and a very faint coloration with KCNS and $K_4Fe(CN)_6$ for iron, after removing the cadmium with hydrogen sulphide, concentrating the filtrate, precipitating with ammonium sulphide and testing the greenish black precipitate for zinc and iron.

On the supposition that the fluorescence is due to one or more of these as an impurity, they were added in small amounts to the pure cadmium sulphate to see if they would then produce phosphorescence. The addition of about 0.1 percent of sodium sulphate made the cadmium sulphate phosphoresce very brightly, nearly as much as the DeHaën material. Addition of zinc sulphate in similar amount made it active but not as much as the sodium. Potassium and

lithium sulphates were tried and they both caused the same light and to about equal degree. Copper and bismuth present in small amounts have no effect, that is, the cadmium sulphate does not phosphoresce.

It has been shown in the case of the phosphorescence of calcium sulphide that the addition of copper, manganese or bismuth cause it to phosphoresce, each with a different color. In the case of cadmium sulphate all the impurities cause the same color. Here then the light is due to the energy of the union of the dissociation products being changed into light by the agency of the impurities, the color being that of the cadmium sulphate. With the calcium sulphide the light is apparently not due to the specific action of the calcium sulphide but is dependent upon the metal impurity that is present, each giving its particular color.

It was observed that the cadmium sulphate which did not show any phosphorescence, the pure material, when exposed to the cathode rays for a long time showed signs of decomposition upon the surface even though it was not active. This indicates two things, first the phosphorescence in cathode rays is not due to decomposition and second that the other metal must be present to cause the energy of the recombination to appear in the form of light. Otherwise, it is set free in some other form, probably heat.

To show how small an amount of an impurity will cause a salt to be phosphorescent there is an interesting case with pure cadmium sulphate. If the dry salt is heated over a Bunsen burner to drive out the water of crystallization the resulting powder is not phosphorescent, but when the salt was dissolved in water which had been twice distilled, the second time from sulphuric acid solution, and this solution was evaporated to dryness in the same way as before, the resulting powder was brilliantly phosphorescent. Plainly there was still something in the water that had this effect. Two hundred cubic centimeters of this water were evaporated in a large platinum dish and the residue left was so small that it could be seen only when the platinum dish was red-

hot. This amount of solid had been dissolved from the bottle in which it had stood over night. It was, however, sufficient to cause the cadmium sulphate to phosphoresce very brightly.

Some of the zinc of the sulphate which showed no phosphorescence in the cathode rays was dissolved in water and a very small amount of sodium sulphate was added evaporated to dryness and ignited over a Bunsen burner until all water was driven off. This showed a bluish white phosphorescence of very short duration. Copper and bismuth present in small amounts cause the same phosphorescence as the sodium. Cadmium sulphate was added in the same way. The first addition caused a very faint bluish white phosphorescence. On increasing the amount of cadmium the light increased in intensity all the time and remained the same color. However, after adding about 1 percent of cadmium sulphate the light became white and tended more towards the yellow although it was still of short duration and not long like the cadmium sulphate. When equal parts of the two were mixed and evaporated down together in this way the resulting phosphorescence is bright yellow like the cadmium sulphate.

A very small amount of manganese added to zinc sulphate made it phosphorescent with a bright reddish yellow color.

That the halogen is given off from the halide salts of some of the heavy metals when exposed to the cathode rays has been shown conclusively by an experiment of Goldstein[1] who placed a piece of copper near some silver iodide exposed to the cathode rays. At first the copper was not fluorescent but some of the iodine given off by the silver iodide united with the copper and formed the cuprous iodide which then fluoresced with its characteristic red-violet color.

This experiment was repeated using copper powder instead of the foil. At first the powder did not give out light, then it became very bright and finally died away again, the surface becoming grayish brown, due to the decomposition of the copper iodide.

[1] Jour. Phys. Chem., 13, 54 (1909).

That there is chemical decomposition by the action of the cathode rays is shown also by the salt turning dark and leaving a colored residue. All of the first group of Wiedemann and Schmidt's classification show this very strongly and it is difficult to draw the line between the first and second group because some of the latter show evidence of decomposition on long exposure. This is the same with cadmium sulphate. When exposed to a heavy discharge for a long time the surface becomes covered with a yellow-brown powder, especially at the edges of the crystals which project up from the surface. In the same way lead sulphate becomes gray on the surface.

That this is not a deposit of particles from the electrode or of organic matter was shown in two ways.

Lead and cadmium sulphates were placed side by side and exposed to the cathode rays at the same time. The former was acted upon more strongly than the latter and the residue was gray while with the latter it was yellow brown. This shows that the lead sulphate is more easily decomposed and that the residue is from the salt and not from the electrode.

This was shown in the second way by placing a sheet of lead with a hole in it over the salt during the exposure. The salt turned brown only where the rays struck the surface. If the coating had been due to organic matter or to particles from the electrode they would have been deposited upon the lead or around the circumference of the salt where the rays struck it and not in the direct path of the rays.

The gray residue from the lead sulphate was insoluble in ammonium acetate so it could not be the oxide but must be the finely divided metal. With the cadmium the residue is the oxide.

In Table III will be found the results of this work, showing the relation between the color of the fluorescence, phosphorescence and thermo-phosphorescence and the color of the light given out when the salt is formed by electrolysis and direct combination.

TABLE III

Salt	Fluorescence	Phosphorescence	Thermophosphorescence	Residue	Electrolysis	Direct combination
NaCl	Whitish	Weak	Blue white	Brown	—	Blue
KCl	White	Weak	Weak violet	Dark violet	—	Blue
Hg_2Cl_2	Orange	—	—	Black	Yellow orange	—
$HgCl_2$	Greenish	—	—	Brown	—	Greenish yellow
AgCl	Green	—	—	Black	Yellowish	Yellow
$CuCl_2$	Greenish	—	—	—	Green	—
$PbCl_2$	Bluish	—	—	Gray	Faint	Faint white
NaBr	Blue white	Weak	Weak	Rose	—	Blue white
KBr	Green	—	Bright	Blue	—	Blue
AgBr	Blue violet	—	—	Black	Weak violet	Faint white
Hg_2Br_2	Orange	—	—	Brown	Orange	—
$HgBr_2$	Orange	—	—	—	—	Yellow orange
$CdBr_2$	Yellow white	Faint	Weak	—	Nothing	Nothing
NaI	White	Weak	Bright	Brown	—	White
KI	Green	—	Weak	Brown	—	Green white
HgI_2	Yellow	—	—	Brown	—	—
Hg_2I_2	Red brown or orange	—	—	Brown	Orange	Orange to red brown
AgI	Blue violet	—	—	Black	Faint	Nothing
PbI_2	Green	—	—	Brown	Yellow	Nothing
Cu_2I_2	Violet red	—	—	Brown	?	Violet red
CdI_2	White	Weak	Strong	—	Yellow white	Nothing
K_2SO_4	Blue	Weak	Bright	—	—	Light blue
$MgSO_4$	Red	—	—	—	Greenish white	—
$PbSO_4$	Blue	—	—	Grayish brown	White	Blue
$ZnSO_4$	Bluish white	White	White	—	White	Blue white
$CdSO_4$	Yellow	Bright	—	Brown	Yellow white	Yellow
Hg_2SO_4	Yellow	—	—	—	Yellow	Nothing
PbO	White	—	—	—	—	—
ZnO	Green	—	—	—	—	Green to blue
CdO	....	—	—	—	—	Yellow
As_2O_3	Green	Faint	—	—	—	Green to blue

In Table III we see the close agreement between the color of the fluorescence and the light given out by chemical union.

With sodium chloride the light given out during chemical combination is the same as that of the thermo-phosphorescence. Since the sodium cannot be used as an electrode there is no result under electrolysis.

The same thing is true with potassium chloride.

The color of the fluorescence of mercurous chloride is the same as the light given out during electrolysis, while that of mercuric chloride is the same as the light given by the burning of mercury in chlorine. This is just as is to be expected since by electrolysis one obtains chiefly the mercurous salt while by d rect union the mercuric salt is formed.

There is an apparent disagreement in the case of silver chloride but in both chemical combination and electrolysis the light was very weak and so it was hard to distinguish the color and for this reason one cannot say with certainty that there is a disagreement.

The same thing is true in regard to copper chloride, the non-agreement may be due to the faintness of the light during electrolysis. This is true also with lead chloride.

Sodium bromide shows agreement between the color of the fluorescence and that of the light given out by direct combination.

Potassium bromide apparently does not show agreement but the reason for this is that the light given out by direct union is a blue green and it is hard to distinguish the exact color.

Silver bromide shows more or less agreement. During electrolysis the film forms so quickly and clings so tightly that there is but a short flash of light at the moment the current is turned on. In causing the direct union of the elements the silver must be heated to a red heat before the union will take place fast enough to give out light. Therefore the faint light due to this chemical combination is hard to distinguish against the bright background of the heated metal.

Mercurous bromide like the chloride agrees with the light given out during electrolysis while the mercuric bromide agrees with the light of direct union.

This again is as it should be since it is the mercurous salt that is formed during electrolysis and the mercuric salt during direct union of the elements.

Cadmium bromide gives no light effect either during electrolysis or direct combination. As mentioned before this may be due to the fact that during electrolysis the solid cadmium bromide is not formed but remains in solution.

Sodium iodide gives white light both during phosphorescence and direct chemical combination.

Potassium iodide shows fairly good agreement, the fluorescent light being green while the light given by direct union is greenish white or light green.

The iodides of mercury do not show very good agreement and this is because of the fact that when iodine and mercury are heated together it will depend upon which element is in excess, whether the mercurous or mercuric salt is formed. If the salt that is formed is treated with water or alcohol, part of it will dissolve and part will not, showing that a mixture of the two is present. Since at the surface of the boiling mercury this element will be in excess it will be the mercurous iodide that will be formed and hence the light given out will be that due to the formation of the mercurous salt. This is apparently what happens. Silver during direct combination with iodine gave no light and during electrolysis in a solution of potassium iodide the light is too faint to enable one to distinguish the color.

Lead iodide does not show agreement as the fluorescence is green while the light obtained during electrolysis is yellow. However, this yellow is toward the green portion of the spectrum and not towards the red.

Cuprous iodide shows very good agreement; the fluorescence, the light from direct union and the little light that is given out during electrolysis are all of the same color.

Cadmium iodide gives the same color during electrolysis as the fluorescence, but direct combination gave no light.

Potassium sulphate gives the same color in fluorescence as in direct combination, the only difference being the depth of the color.

Magnesium sulphate does not agree and the reason as given before is that during electrolysis in concentrated sulphuric acid the light given out is due to a static discharge and not to the formation of magnesium sulphate. No light was obtained by a direct union of magnesium and the sulphate group.

The fluorescence of lead sulphate is the same color as the light from the union of lead with the sulphate group. The light given out by the electrolysis of sulphuric acid with a lead electrode is too faint to be certain of the color but appears white although the blue would probably come out if the light could be made stronger. When concentrated acid is used the light becomes greenish white, due to a static discharge.

Cadmium sulphate gives the same light during fluorescence, direct union and electrolysis, the only difference is that in electrolysis the color is a lighter yellow.

Mercurous sulphate gives the same light during electrolysis as the fluorescence but the direct union gives a negative result. This is due probably to the fact that one cannot heat the mercury high enough to make it react with the sulphate group fast enough to give out light.

Zinc oxide gives a green light during fluorescence, during direct union brought about in a stream of oxygen by boiling the metal by means of a blast lamp or during the action of sodium peroxide. The blue light sometimes given out by the action of the sodium peroxide may be due to a second light effect from the sodium peroxide itself.

Cadmium oxide burns with a yellow flame but is not fluorescent.

Arsenic trioxide gives a green light both during fluorescence and direct union of the metal with oxygen, although the light may be blue if the oxygen supply is increased.

There are three possible sources for the light given out by mercury salts under the cathode rays.

(1) Formation of the mercurous salt by the direct union of the elements.

(2) Formation of the mercuric salt by the direct union of the elements.

(3) Change of the mercurous to the mercuric salt.

It is possible that each of these may give out light and may have its own characteristic color.

By electrolysis with a mercury anode one obtains the mercurous salt and the light due to its formation. By the direct union of the elements one obtains usually the mercuric salt. An attempt was made to heat the mercurous salt in the presence of an excess of the halogen to convert it into the mercuric salt and see if any light was given out during the reaction. But the mercurous salt breaks down so easily and at such a low temperature into a mixture of mercury and the mercuric salt that the temperature could not be raised high enough to cause the reaction between the halogen and the mercurous salt to go rapidly enough to give out light.

After the mercurous salt breaks up and the temperature is raised the reaction takes place between the halogen and the mercury that has been set free and gives out the light due to this reaction.

Summary

In this work we have obtained the following results:

(1) There is a definite close relation between chemical action and phosphorescence.

(2) A number of salts prepared by electrolysis give off light during their formation.

(3) A number of salts prepared by the direct union of the metal with the acid radical give off light during their formation.

(4) In the case of sodium and potassium it was shown that the light given out by the slow union with the acid radical is different from that given out by rapid union

(5) The color of phosphorescence and thermo-phosphorescence is the same as that of this slow union.

(6) In nearly every case the phosphorescent light is of the same color as the light given out by chemical combination.

(7) Some salts said to be phosphorescent were found not to be so when pure.

(8) Some salts which were said not to show decomposition on exposure to cathode rays were found to do so on long exposure.

(9) Some of the salts which did not show phosphorescence were made to do so by the addition of other salts as impurities.

(10) Cadmium sulphate breaks down upon long exposure to the cathode rays and leaves a residue of the oxide.

(11) Lead sulphate breaks down in the cathode rays and leaves a residue of finely divided lead.

(12) Metathetical reactions, by which a number of these salts were formed in solution, show no ight effect.

(13) The decomposition of some of the salts by metallic sodium showed no light effect.

(14) The electrolysis of some of the fused alkaline halides with an alternating current showed no characteristic glow like that which Lenard found when these salts were heated on a platinum wire in the flame.

(15) Sodium peroxide shows fluorescence and phosphorescence under the action of cathode rays if vacuum is maintained by continuous pumping.

(16) The fluorescence of aluminum oxide under the cathode rays is due to the presence of sodium in the form of the peroxide or the aluminate.

This work was suggested by Professor Bancroft and has been carried out under his direction. The author takes this opportunity of expressing appreciation of his many suggestions and generous interest in the work. He also thanks the Department of Physics for the use of apparatus in facilitating the work.

Cornell University,
May, 1909

NEW BOOKS

Studien zur Lehre von den kolloiden Lösungen. *By T. Svedberg. (Nova Acta Regiae Societatis Scientiarum Upsaliensis. Ser. IV, Vol. 2, No. 1.) 22 × 28 cm; pp. vii + 160. Upsala: Akademische Buchdruckerei, 1907.*—Bredig's method of obtaining colloidal metals by means of an arc under the surface of a liquid works well with methyl alcohol and ethyl alcohol; but with many organic solvents the liquid itself is decomposed and carbon is set free. The author connects his electrodes with the secondary wires of an induction coil and places a glass condenser in parallel with them. One electrode consists of granular metal or of metal strips. This apparently gives him a universal method by which any metal can be obtained in colloidal form. The disintegration is due to an oscillatory arc discharge. The most favorable conditions are those in which the capacity is as large as possible while the self-induction, the ohmic resistance, and the length of spark are kept as small as possible. In the different groups of the periodic system the disintegration increases rapidly with increasing atomic weight. The decomposition of the liquid is greatest with the positive metals such as calcium and magnesium; and with those which have catalytic properties such as cobalt, nickel, and platinum.

One of the very interesting things in the paper is the account of the preparation of colloidal metals of the alkalies and of the alkaline earths. Ethyl ether and pentane were used as liquids in an atmosphere of hydrogen. With potassium, rubidium and caesium it was necessary to work at temperatures approximating —100° C.

"In the group, sodium, potassium, rubidium and caesium, there are some very interesting regularities. In the first place, there are relations between the atomic weight and the color of the colloidal solutions. With increasing atomic weight the color moves toward the red end of the spectrum. Colloidal sodium is violet—very like a solution of potassium permanganate—potassium is blue, rubidium blue with a touch of green, and caesium bluish-green, these colors being those of the smallest particles. In the second place, the color depends on the size of the metallic particles. With increasing coagulation the particles become larger and the color moves toward the red end of the spectrum. It has often been pointed out that there is no simple relation between the size and the color of the particles, but it seems to me that in this case this relation is quite unmistakable.

"There is also a surprising agreement between the color of the colloidal solution and that of the metal as vapor. In the literature there are only brief and incomplete notes on the colors of the vapors of the alkali metals. In fact, the color of caesium vapor is not a matter of record, so far as I know. The agreement is very good for sodium and rubidium. Potassium vapor is bluish-green at low temperature and the larger particles of colloidal potassium are also bluish-green; but the smallest particles of colloidal potassium are blue. It would be of great interest to determine the colors of the vapors of the alkali metals at different temperatures, to determine the absorption spectra, and to compare these last with those of the colloidal solutions. A determination of

caesium vapor would be especially important as it would show whether the relations mentioned apply to this metal as well. Of course there would be serious difficulties in carrying out such an investigation for these vapors attack almost all vessels."

In the second section of the volume, the author considers the question of stability and finds that there are well-defined critical temperatures and that these temperatures are raised by the addition of small amounts of a non-colloidal third substance.

The third section deals with the Brownian movements. The author gives the particles a constant movement in one direction, thus changing the oscillations into a wave-form of curve. This simplifies the measurements and the author finds that the velocity of the particles is about one hundred times that of the electrical migration under a potential drop of one volt per centimeter. He therefore considers that the Brownian movements cannot be the result of electrical phenomena. After considering other possibilities, the author decides that the Brownian movements are due to the actual oscillations of the molecules as required by the kinetic theory of gases.

Whether one accepts this last conclusion or not, there is no question but that this is a very important investigation, and one which reflects great credit on the author. *Wilder D. Bancroft*

Oeuvres de Pierre Curie, *Publiées par les Soins de la Société Française de Physique. 16 × 25 cm; pp. xxii + 621. Paris: Gauthier-Villars, 1908. Price: paper, 22 francs.*—This volume of six hundred pages contains the complete works of Pierre Curie. At first sight this does not seem a large output for an active scientific career extending over twenty-seven years; but the work is not of a kind to be measured by pages. At no time did Curie have a large number of students or an adequately equipped laboratory. All his life he interested himself in difficult problems of such a nature that the results of a great deal of work could be presented in relatively few words. The work on crystallography and on radioactivity may serve as an illustration. Then, too, Curie was a man who thought long about a subject before he published anything on it, and if some one anticipated him he did not publish at all. It is a matter of opinion whether an intense yearning for perfection in each publication is an unmixed blessing; but one cannot help admiring the man who has it and who lives up to it in these days when so many of us go to the opposite extreme.

Curie's papers deal with four general topics: crystallography; reduced equations; magnetism; and radioactivity. The last group is the one which has attracted the most attention and on which Curie was working when his career was cut short; but it would be a great mistake to consider the earlier work as unimportant. To take but a single instance, the paper on the magnetic properties of substances at different temperatures is a masterly piece of work and will some day receive a great deal more attention than has yet been bestowed upon it.

The whole world is familiar with the details of Curie's untimely death; but it has not known until now, about his unsatisfied longings for more adequate facilities. It is pathetic the way in which Curie was offered decorations when what he wanted was a laboratory. *Wilder D. Bancroft*

Essai sur la Notion de Théorie physique de Platon a Galilée. *By Pierre Duhem. Extrait des Annales de Philosophie Chrétienne. 16 × 25 cm; pp. 143. Paris: A. Hermann, 1908. Price: paper, 5 francs.*—"According to Plato the heavenly bodies move with a circular, uniform and entirely regular[1] motion. He places this problem before the mathematicians: What circular, uniform and entirely regular motions must be assumed in order to account for the apparent motion of the planets?

"This aim of astronomy is here presented with great clearness. This science combines circular and uniform movements in such a way as to give a resultant motion corresponding to that of the stars. When the geometrical construction assigns to each planet a motion resembling that which is actually seen, the goal of the astronomer has been reached for his *hypotheses have accounted for the phenomena.*"

"Though the astronomer may be fully satisfied when the hypotheses, which he has devised, account for the phenomena, has not the mind of man a right to ask for something more? Can it not discover and analyze some characteristics depending on the nature of the heavenly bodies? May not these characteristics enable him to point out certain fundamentals to which the astronomical hypotheses must necessarily conform? Ought it not be possible to exclude certain hypotheses as not conforming to these fundamentals even though these hypotheses account for the phenomena?

"In addition to *the method of the astronomer*, so clearly defined by Plato, Aristotle maintains the existence and legitimacy of other criteria; he calls this *the method of the physicist.*"

"Aristotle insists that the universe is spherical, that the celestial bodies are solid, that each one of them has a circular and uniform motion around the centre of the universe, and that this centre is occupied by the stationary earth. These are restrictions which he imposes on the hypotheses of the astronomers and he would not hesitate to reject any combination of movements which seemed to violate any of these conditions. He does not impose these conditions because he believes them indispensable in accounting for the phenomena which have been observed. According to him they are made necessary by the perfection of the essence from which the heavens are formed and by the nature of circular motion. While Eudoxius and Calippus adopt the method of the astronomer and check their hypotheses by seeing whether they account for the phenomena, Aristotle undertakes to restrict the choice of hypotheses by means of certain propositions justified by speculations on the nature of matter: his method is that of the physicist."

In this volume Duhem sketches the developments of these two points of view from the time of Plato to that of Galileo. The matter is of fundamental importance and the question whether the particular restrictions imposed by Aristotle are correct is one of entirely secondary importance. That the problem is not purely an academic one is shown by the fact that Hipparchus was able to account for the apparent motion of the sun round the earth by two distinct hypotheses. Here again it is quite unimportant that we now know that neither hypothesis was right. In a different form the difference of opinion between

[1] Always in the same direction.

Plato and Aristotle is a live question to-day. Most physicists and chemists recognize as one goal the representation of phenomena by means of a kinetic hypothesis. Others are searching—so far in vain—for some criterion which will enable them to exclude the kinetic hypothesis from the list of permissible hypotheses, quite irrespective of the success with which the kinetic hypothesis may represent the facts. Until the appearance of Svedberg's "Studies on Colloidal Solutions," Ostwald was unquestionably an Aristotelian. It is not certain whether he still is or not.

In the summary Duhem says:

"Many philosophers since Giordano Bruno have reproached André Osiander bitterly for the preface which he wrote for the book of Copernicus. The advice given to Galileo by Bellarmine and by Urban VIII has been treated with little less severity ever since it was published. However, the physicists of our time have been more careful than their predecessors in their examination of the exact value of the hypotheses made use of in astronomy and in physics. They have seen many things change to illusions, in spite of having been considered as certainties not very long ago. They are obliged to recognize and to declare to-day that logic was on the side of Osiander, of Bellarmine, and of Urban VIII and not on the side of Kepler and of Galileo; that the former had understood the exact limitations of the experimental method while the latter had been confused in regard to it.

"The history of science nevertheless exalts Kepler and Galileo whom it places in the ranks of the great reformers of the experimental method, while it does not pronounce the names of Osiander, of Bellarmine and of Urban VIII. Is not this because those, who had a false idea of the value and limitations of the experimental method, have developed this method much more and much better than those, whose appreciation of it had been at first more exact and more thorough?"

Wilder D. Bancroft

Traité de Physique. *By O. D. Chwolson. Ouvrage traduit sur les Éditions russe et allemande par E. Davaux. Édition revue et considérablement augmentée par l'Auteur, suivie de Notes sur la Physique théorique par E. Cosserat et F. Cosserat. Avec une Préface de E.-H. Amagat. Tome premier, quatrième fascicule. 16 × 25 cm; pp. 873–1092. Paris: A. Hermann, 1908.*—This volume is devoted entirely to acoustics and while there is not as much of immediate interest to the physical chemist in it as in some of the preceding numbers, the book contains a good deal which can be read with profit.

On p. 902 we find the following general remarks on acoustics:

"That part of physics which we call acoustics deals with the phenomena of sound. It has some distinct peculiarities. In the first place it is characterized by the lack of any special hypothesis of great importance, such as the hypotheses on which rest the study of radiant energy, of heat energy or of electrical energy. The vibrations of matter, which are closely connected with the phenomena of sound, are usually to be perceived by our senses. We can see them or feel them and we have no doubt of their reality. In so far as acoustics is a study of a definite group of phenomena, it approaches more closely than the other divisions of physics to that ideal towards which science tends, and according to which the facts of nature are accounted for completely by the principles

of mechanics without introducing any hypothetical substance, any particular property of matter or any special force of nature.

"From the point of view of mechanics, *acoustics is a chapter in the theory of elasticity*, which treats the different cases of the propagation of vibratory motion in a displaceable medium. The object of experimental acoustics is to reproduce the conditions, which have been studied theoretically, and to verify the results obtained. The phenomena of sound are also extremely interesting from two other points of view. In the first place they are perceived by the ear, though only between certain limits, and they produce impressions of the particular nature called impressions of hearing. This fact exercises a great influence on the method of observation of phenomena reproduced in acoustics. We usually judge of the existence of these phenomena from the subjective information furnished by the ear. A physiological element thus appears in acoustics; we must consider the structure of the ear and the way in which the sound-vibrations are perceived by it. In the second place, acoustics is connected with music, one of the most important and wide-spread of the arts. The connection between acoustics and music is very much more close than that between optics and painting, for instance."

On p. 934 is given Tyndall's explanation in regard to the acoustic transparency of the air.

"The question of the acoustic transparency of the air, in other words of the distance at which a sound can be heard in open air, under definite conditions, is one which is of great importance even from the practical point of view. This question has been studied very carefully by Tyndall. Before his time people believed that rain, snow, hail, and especially fog decreased the acoustic transparency of the air very much and that the acoustic transparency was greatest on clear days when the optical transparency was greatest. Tyndall determined on different days the distances at which sirens, steam whistles and cannon shots, coming from a definite place on the English coast, could be heard over the surface of the sea. His very first experiments showed that these distances varied from 20.4 kilometers to 3.2 kilometers in the course of a few days. Tyndall succeeded in discovering the cause of these important variations. He found that the *acoustic transparency of the air depends entirely on its degree of homogeneity*. Rain, snow, hail and fog do not necessarily make the air heterogeneous and consequently the air may have a high acoustic transparency in a time of the thickest fog. But when there are heterogeneous strata in the air, especially vertical ones, in which the velocity of sound is not the same, the acoustic transparency of the air decreases enormously because the sound is reflected from the surfaces separating the strata. Thus, on a clear day, when the sun is shining there are ascending currents of hot air and at the same time descending currents of moist air (above rivers, swamps, etc.). These decrease the acoustic transparency of the air very considerably. In this way we can account for the fact that air, which is very transparent optically, may be acoustically very opaque."

On p. 945, under reflection of sound, we get Reynolds's explanation of the same phenomena in which he lays stress on a vertical inhomogeneity instead of on a horizontal inhomogeneity. According to Reynolds the sound is refracted upwards and may afterwards be refracted downwards in case con-

ditions are right. This would make it possible that a whistling buoy, for instance, might be heard distinctly at a certain point and could not be heard as the observer approached somewhat nearer the buoy. The reviewer has heard of cases of this sort along the Maine coast. Of course, the theory of Reynolds is merely an extension of Tyndall's theory. Any inhomogeneity in the air, whether vertical or horizontal will cause a reflection or refraction of sound.

On pp. 936–939 is given an account of explosion waves. The author seems to be more familiar with the work of Mallard and LeChatelier than he is with that of Dixon, and his bibliography of the subject is also incomplete. The author quotes Duhem's theory in regard to explosion waves, but evidently does not look upon it with much approval. *Wilder D. Bancroft*

A Text-Book of Inorganic Chemistry. *By A. F. Holleman. Issued in English in coöperation with Hermon Charles Cooper. Third English edition, partly rewritten. 15 × 23 cm; pp. viii + 488. New York: John Wiley & Sons, 1908. Price: $2.50.*—In this volume osmotic pressure is taken up just after hydrogen peroxide, dissociation after iodine, electrolytic dissociation after fluorine, the phase rule after sulphur, thermochemistry after tellurium, the law of Dulong and Petit after lead, solubility curves after ammonium salts, spectroscopy after barium, and electrochemistry after mercury. The book is a physical chemistry sandwich. The salts of sodium, copper and silver are not reached till the last third of the book, quite a while after the student has learned about germanium. The solubility product and the theory of electrolytic dissociation are discussed before the student has learned about a single metal. The formulas for reaction velocity are given when the only elements, which have been discussed, are oxygen, hydrogen, chlorine, bromine and iodine. This may be a helpful way of introducing the student to the subject of chemistry, but the reviewer feels skeptical about it.

The reviewer has been used to seeing the term "Aq" used to denote a large amount of water and it seems a pity to write "*n* Aq," p. 57, to denote water of crystallization. In the statement of the phase rule, p. 114, there is nothing to show that this is true only when the variables to be considered are the components, the pressure and the temperature. Three pages are given to the bearing of the solubility product upon the solubility of sulphides, but there is nothing to show that one may have HS-ions with hydrogen sulphide. It seems to the reviewer as though the student might have a good deal of trouble with the following paragraph, p. 121:

"As soon then as the concentration of the S-ions becomes so small (because of the reduction of the ionization of hydrogen sulphide by the H-ions of the acid) that it makes the value of *ab* smaller than that of the solubility product for copper sulphide, no precipitate will be formed. If, however, the liquid is diluted, the concentration of the H-ions decreases; then if hydrogen sulphide is passed in, the concentration of the S-ions increases. The value of the solubility product can in this way be exceeded, in which event copper sulphide will be precipitated." The student will be bothered by the fact that adding hydrogen sulphide means adding two hydrogen ions for every sulphur ion and it will seem to him that he is increasing the concentration of hydrogen ions and is therefore preventing the precipitation of copper sulphide. The

fallacy in this reasoning is a simple one, but it seems a pity to make the student struggle with it.

On p. 143 it is not clear to the reviewer that sulphur trioxide is absorbed most readily by 97–98 percent sulphuric acid because this solution "has a minimum of vapor tension, which is very low." There seems to be a confusion between total pressures and partial pressures. In any case it would have been better to have admitted frankly that we don't know at all why this concentration acts as it does.

On p. 286 the author speaks of lead persulphate, $Pb(SO_4)_2$, when he means plumbic sulphate. Lead persulphate is PbS_2O_8 and has very different properties from plumbic sulphate.

On p. 316 we have another confusion of ideas. "It is found that a perfectly sound crystal of $Na_2SO_4.10H_2O$ does not effloresce, but that when efflorescence has begun at any point it spreads over the crystal. The phase rule gives a satisfactory explanation of this phenomenon. We have in the Glauber's salt two substances, Na_2SO_4 and H_2O; in the case of a perfectly bright crystal exposed to the air we have only two phases, $Na_2SO_4.10H_2O$ and H_2O (moisture of the air). According to the equation $F + P = S + 2$ we still have in this system two degrees of freedom, *i. e.*, the pressure of the water vapor and the temperature can both be settled arbitrarily (within certain limits). If, however, some dehydrated salt is present, the number of phases is three; then there is only one degree of freedom, or, in other words, every temperature has only one corresponding pressure and inversely every pressure only one corresponding temperature. Accordingly it is only permissible to speak of the well-defined vapor tension of a salt with water of crystallization when a second solid phase is tacitly admitted to be present; for then only is the number of degrees of freedom reduced to one."

The general statement is correct but it has nothing to do with the experimental fact which apparently gave rise to it. The phase rule does tell us that a hydrated salt can coexist with vapor at a given temperature over a range of pressures, but it does not tell us anything in regard to the fact, described by Faraday, that a perfectly sound crystal of Glauber's salt does not necessarily effloresce when the partial pressure of the water vapor is brought below the dissociation pressure. In Faraday's experiment, he was not dealing with a case of reversible equilibrium. The phase rule tells us nothing about the possibility of supercooling, supersaturation, etc., etc.

On p. 319 the reviewer is quite unable to understand what the author means.

"The apparently very simple process of electrolysis of a sodium chloride solution, expressed ordinarily by the equations

$$NaCl = Na + Cl \text{ and } Na + H_2O = NaOH + H$$

is in reality rather complicated. The resulting sodium hydroxide is itself an electrolyte and is broken up into sodium and hydroxyl ions. The sodium thus liberated immediately forms new hydroxide, but without increasing the alkalinity, since it was previously present as sodium hydroxide. The practical result therefore is a decomposition of water and a consumption of electrical power proportional to the latter."

The practical result of electrolyzing aqueous caustic soda is the decomposition of water, but that is not the case when electrolyzing a concentrated sodium chloride solution. Also, so far as the reviewer knows, nobody makes sodium amalgam commercially and recovers the mercury by distillation, p. 318.

The reviewer would like to say something about the alleged argument on p. 336 to show that there is no difference between solvent and solute, but it would not do any good and, after all, the matter is one on which a difference of opinion is permissible.

Though one cannot conscientiously praise the arrangement and though a good deal of the physical chemistry is unfortunate either in wording or in application, it must be recognized that the book contains a large amount of useful information and that in some cases one runs across information which is not generally familiar. As an instance of this, the reviewer takes pleasure in quoting the following passage from p. 181.

"A solution of ferrous sulphate is precipitated with an excess of sodium hydroxide and warmed; if hydroxylamine (or one of its salts) is now added to the green ferrous hydroxide, red ferric hydroxide is formed very quickly, the hydroxylamine being reduced in this alkaline solution to ammonia. On acidifying, an acid solution of a ferric salt is obtained; if this is treated with a hydroxylamine salt, it is suddenly decolorized because of reduction to ferrous salt, the hydroxylamine being now in the oxidized condition in the acid solution."

The translator has done his work well. *Wilder D. Bancroft*

Gesättigte Salzlösungen vom Standpunkt der Phasenlehre. *By Ernst Jänecke. 17 × 24 cm; pp. ix + 187. Halle: Wilhelm Knapp, 1908. Price: paper, 9 marks.*—The book is based on lectures given by the author in 1906 at the Polytechnic in Hanover. The subject is treated under the headings: diagram for water and for other one-component systems; classification of salt solutions according to the phase rule; saturated solutions of one salt which crystallizes always without water of crystallization, one salt and water with the salt separating as hydrated or anhydrous salt; solutions of two salts with a common ion, no solid solutions possible; occurrence of solid solutions in saturated solutions of two salts with a common ion; solutions of a salt in basic and acid solvents; aqueous solutions of three salts having the same ion in common; aqueous solutions of four salts having the same ion in common; solutions of reciprocal salt pairs; solutions of reciprocal salt pairs when there is a fifth and sixth salt present as solid phases; salt solutions with three different cations and two anions or three different anions and two cations.

The special feature of the book is the graphical representation of the different equilibria. It seems to the reviewer that it would have been a good plan to have added a chapter on methods of determining the composition of solid phases. The diagrams for distinguishing between a double salt, a solid solution and a mixture can hardly be repeated too often. *Wilder D. Bancroft*

Die edlen und die radioaktiven Gase. *By William Ramsay. Vortrag, gehalten im Österreichischen Ingenieur-u. Architekten-Verein zu Wien. 16 × 24 cm; pp. 39. Leipzig: Akademische Verlagsgesellschaft m. b. H., 1908. Price: linen, 1.40 marks; bound, 1.80 marks.*—The author starts with the experiments

of Priestley and of Scheele on the composition of the atmosphere, gets by quick stages to comparatively recent times, and gives a very readable account of many of the steps in connection with the discovery of the inert gases.

The following passage is interesting whether we agree with it or not:

"We consider it probable that the emanation, which has proved indifferent to all chemical reagents, is to be included in the list of the noble gases. If this assumption is correct the emanation must have a high atomic weight for in this group there are only two vacant places; one with the atomic weight 128 + 45 = 173, and one with the atomic weight 128 + 90 = 218. Now it seems probable that, if an element should under any circumstances acquire the power to decompose, its decomposition products would be elements of the same group. Since helium, neon, and possibly argon are among the gaseous decomposition products of the emanation, since the decomposition is not changed by water, copper sulphate solution or anything, and since lithium is probably one of the products of a copper sulphate solution which has been exposed to the emanation, it seems not impossible that in the first case only a portion of the emanation yields such products as helium and neon while a much larger fraction, about 92 percent of the whole amount, serves as a source of energy....."

Wilder D. Bancroft

La Réfractométrie et ses Applications Pratiques. *By D. Sidersky. (Encyclopédie scientifique des Aide-Mémoire publiée sous la direction de M. Léauté.) 12 × 19 cm; pp. 172. Paris: Gauthier-Villars. Price: paper, 2.50 francs; bound, 3 francs.*—In the preface the author says:

"The determination of the index of refraction of liquids has assumed considerable importance in the last few years and the refractometer has become of great use to the chemist. Just as fast as the physicists and the manufacturers have improved their instruments, making them more accurate, the chemists have increased their investigations in regard to all possible indices of refraction in order to use these constants in the analysis of organic substances and especially in determining cases of adulteration in cases where the ordinary methods of chemical analysis often fail.

"We have thought that it would be useful to combine in a volume of the *Encyclopédie scientifique des Aide-Mémoire* the most striking of these investigations and improvements, pointing out first the theory of refraction, then the different methods used for the determination of the indices, and lastly the practical applications to analytical chemistry."

The headings of the chapters are as follows: refraction of light; determination of index of refraction; new refractometers; practical applications of refractometry; numerical tables. In the last chapter, there are tables giving data for glasses, solids, liquids, oils, fatty substances, essential oils, gases and vapors.

Wilder D. Bancroft

Polarization et Saccharimétrie. *By D. Sidersky. Encyclopédie Scientifique des Aide-Mémoire, publiée sous la direction de M. Léauté. Deuxième édition, revue et augmentée. 12 × 19 cm; pp. 168. Paris: Gauthier-Villars; Masson et Cie.*—In the preface to the second edition the author says:

"Since the appearance of the first edition many experimental data have been collected in regard to the rotatory power of organic substances and these

data necessitate a modification of some matters previously given. I have taken account of this, so far as possible, by revising the values given in the tables of specific rotatory powers. I have added a table of multirotations and I have changed the different saccharimetric tables, basing them on the new official standard weight of 16.29 adopted in French saccharimetry.

"In the descriptive part I have called attention to some new forms of apparatus as well as to improvements in old forms. In the analytical part I have indicated the new methods of analyzing sugar beets, commercial glucoses, etc. A new chapter has been added to show the use of the rotatory power as a means of analyzing some interesting substances containing alkaloids or other optically active compounds." *Wilder D. Bancroft*

Explication mécanique des Propriétés de la Matière, Cohésion, Affinité, Gravitation, etc. *By A. Despaux. 14 × 23 cm; pp. 352. Paris: Felix Alcan, 1908. Price: paper, 6 francs.*—The author starts with the hypothesis of a helicoidal molecule and discusses the molecular constitution of matter; the energies and properties of matter due to the rotation of the molecules; the energies and properties of matter due to the translatory motion of the molecules; chemical affinity; gravitation; hypnotic suggestion, and various other matters. As is often the case in books of this class, the author is not very careful in regard to his facts. On p. 110 he states that a layer of oil keeps water from evaporating because the oil is impermeable to water. As a matter of fact the partial pressure of water vapor is practically not affected by the oil at all, provided we wait until equilibrium is reached. He also claims that air cannot pass through oil to water, though the fallacy of this was shown in Ostwald's laboratory over twenty years ago.

On p. 160 DeSaporta is quoted as the authority for the statement that no molecule with more than twelve atoms can exist as vapor; being so heavy it is decomposed by heat. It is evident that the author has never distilled toluene.

On p. 194 it is stated that a copper sulphate solution is the best electrolytic conductor known.

The author rejects the electrolytic dissociation theory entirely, p. 195. He looks upon the current as an independent thing which starts the positive radical corkscrewing through the solution. No distinction is made between the transference of the ions by the current and the phenomenon of electrical endosmose. Of course such a quantitative relation as Faraday's law does not appeal to the author as being of any importance. *Wilder D. Bancroft*

Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischen Wege. *By Jaroslav Formánek unter Mitwirkung von Eugen Grandmougin. Zweite, vollständig umgearbeitete und vermehrte Auflage. Erster Teil. 16 × 24 cm; pp. viii + 257. Berlin: Julius Springer, 1908. Price: paper, 12 marks.*—As the title shows, the author advocates the use of the spectroscope in the investigation and determination of organic dyes. Ordinary methods of analysis are nothing like so satisfactory when it comes to identifying the same dye sold under different names or when it is a matter of detecting impurities or adulterations. In cases where the absorption spectra of two dyes are very similar under ordinary conditions, the use of another solvent will often cause a sufficient

divergence of the absorption spectra, p. 7, to make it possible to distinguish between the two dyes.

On p. 16 the author gives an interesting circular diagram to show the relation between the color of a solution and its absorption spectrum. On p. 20 there is a discussion of Kundt's rule as to the effect of the solvent on the absorption spectrum. In 910 cases examined by the author only 485, or 53 percent, conformed to Kundt's rule. In certain cases the change from water as solvent to ethyl alcohol displaces the absorption bands in one direction while the change is in the opposite direction when amyl alcohol is substituted for water.

The author points out, p. 25, that a thin layer of a concentrated solution will not give the same absorption spectrum as a thick layer of a dilute solution if any hydrolysis takes place. He records several cases in which the absorption spectrum of a freshly-prepared solution varies progressively with the time for a short while. It seems as though this might be studied as a case of reaction velocity.

On p. 31 the author records a most extraordinary statement in regard to the behavior of methylene blue and methyl violet.

"If we mix dilute solutions of methylene blue and of methyl violet 6 B and determine the position of the main absorption bands of the two dyes, we find that the absorption band of methyl violet is no longer in its original position at λ 593.5 but has been moved somewhat to the left by the influence of the absorption band of methylene blue and is now at about γ 595.0. The greater the amount of methylene blue and the less the amount of methyl violet, the more is the absorption band of the methyl violet moved from its original place and *vice-versa*. This displacement has definite limits, those for methyl violet being λ 500.5 and λ 590.7.

"The same phenomenon takes place if the two solutions of methyl violet and of methylene blue are placed one behind the other in separate vessels and are then examined with a spectroscope."

It is a pity that the author did not go into this matter more in detail, because the reviewer has no hesitation in saying that the facts are impossible as stated.

On p. 97 there is the interesting statement that all dyes, which fluoresce in other solvents, lose their fluorescence when dissolved in aniline.

The author presents his subject under the headings: introduction; the spectroscope; general relations between color, absorption, fluorescence, and constitution of dyes and colored compounds; relations between constitution and absorption spectrum for some groups of dyes; di- and tri-phenylmethane dyes; quinone imide dyes; fluorindine and triphendioxazine; acridine dyes; anthraquinone dyes. *Wilder D. Bancroft*

Traité complet d'Analyse chimique, appliquée aux Essais Industriels. *Par J. Post et B. Neumann. Avec la collaboration de nombreux chimistes et spécialistes. Deuxième édition francaise entièrement refondue. Traduite d'après la troisième édition allemande et augmentée de nombreuses additions. Par le L. Gautier. Tome second; premier fascicule. 16 × 25 cm; pp. 199. Paris: A. Hermann, 1908. Price: paper, 6 francs.*—This volume contains a chapter on lime, mortar,

cement and plaster; one on ceramic products; and one on glasses and glazes. The subject of glazes is a fascinating one which will certainly be taken up by the physical chemist some day and then he will find the information in this book of great value to him. It is well known that the high price of artistic potteries is due in part to the uncertainty of the process, the number of successful pieces being relatively small. This is merely the result of doing things in a haphazard way without paying careful attention to the temperature and to the composition of the gases in contact with the ware. Some day these things will be run as they should be and then we shall hear much less about the impossibility of controlling conditions. *Wilder D. Bancroft*

Tables and Diagrams of the Thermal Properties of Saturated and Superheated Steam. *By Lionel S. Marks and Harvey N. Davis 16 × 23 cm; pp. 105. New York: Longmans, Green & Co., 1909. Price: bound, $1.00 net.*—"The tables of the properties of saturated steam which have appeared up to the present time have all been based upon the classic investigations of Regnault, carried out more than sixty years ago. It has been apparent for some time that the total heats of dry and saturated steam, as determined by those admirable researches, are below the correct values. The great difficulty in obtaining steam which is exactly dry and saturated has not been appreciated until very recently; and it is undoubtedly true that Regnault was investigating steam containing a small amount of moisture when he thought that he was dealing with dry steam. Fortunately, the recent investigations of Dieterici, Smith Griffiths, Henning and Joly give a trustworthy body of new values of the total heat of dry steam at pressures below atmospheric pressure, while the method recently elaborated by Davis, when applied to the throttling experiments of Grindley, of Peake, and of Griessmann, gives remarkably accordant determinations at pressures above atmospheric pressure. The table which we have prepared is based entirely upon these new values, and is probably correct to one-tenth of 1 percent within the range of steam pressures usual in engineering practice. Regnault's formula gives results which are too high by 18 B. t. u. at 32° F, too low by 6 B. t. u. at 275° F, and again too high at 380° F, the error increasing rapidly at higher temperatures.

"The investigations of Knoblauch, of Thomas and of Henning are the necessary basis for any determinations of the properties of superheated steam. These investigations have been subjected to a careful analysis, both as to the probable errors resulting from the methods of experimentation, and also as to the relation of the experimental results to the values deduced from thermodynamic theory, so far as this latter throws any light on the matter. Where the results of the separate investigations are not closely accordant, a critical estimate has been made of the relative values to be given to each, in the region under consideration. The properties of superheated steam are tabulated for every pound pressure, and for every ten degrees of superheat, within a range which exceeds present practice. All the information relating to superheated steam of any pressure is given on one double-page, an arrangement which permits the immediate finding of any desired quantity. Supplementary tables extend the superheated steam table to very high temperatures and give the properties of water, metric conversion factors, Naperian logarithms and other quantities.

"Beside the tables, we have prepared two large diagrams showing the properties of saturated and superheated steam. These diagrams can be used, instead of the tables, for finding the total heat, entropy and specific volume of steam of any known quality or superheat (within an extended range), but their chief purpose is to facilitate certain calculations. In consequence of the variation of the specific heat of superheated steam with both pressure and temperature, the solution of commonly occurring problems involving superheated steam is either laborious or approximate. If the tables are arranged in such a manner as to aid the solution of problems of one class, they become inconvenient for other purposes. The total heat-entropy diagram, devised by Mollier, makes it possible to solve immediately many of the problems which arise in connection with either saturated or superheated steam. A total heat-pressure diagram, showing specific volumes, permits the solutions of problems involving volumes. By the use of the two diagrams, either separately or together, a large number of the steam problems occurring in the design of engines and turbines, or in connection with the flow of steam, or its throttling, can be solved without any calculation. These two diagrams have been plotted with great care from the data given in the tables, and should prove useful to all engineers or students engaged in making calculations which involve saturated or superheated steam."

Wilder D. Bancroft

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